Electronic Supplementary Material (ESI) for Nanoscale.

Polypyrrole and Activated Carbon Enriched $MnCo_2O_4$ Ternary Composite as Efficient Electrode Material for Hybrid Supercapacitors

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Supporting Information (SI)

1. Electrode preparation method

The electrodes were prepared by blending the synthesized active material, PVDF (binder), and carbon black (conductive element) in a ratio of 8:1:1 to get consistent slurry with the addition of N-Methyl-2-pyrrolidone (NMP). Nickel foam with area of 1 cm^2 was then coated with this slurry and dried at 60 ℃ overnight. The separator (Whatman paper) wetted by 6M KOH electrolyte was sandwiched between the two electrodes (cathode and anode) and pressed using a hydraulic press to get the desired cell configuration.

2. Electrochemical measurements

The capacitive response of the electrode material corresponding to a voltage window of -1 to +1V was evaluated from CV and GCD in 2-electrode configuration. The EIS analysis was carried out for 10^5-0.1 Hz of frequency at open-circuit voltage. For asymmetric supercapacitor, the voltage range was 0-1.6 V. The Formulae used for determining various parameters such as specific capacitance, energy density, and power density has been provided in **Table S1**.

Table S1: Formulae used for finding various parameters.

Parameter	Formula	Terms used
Bragg's law	$2d\sin\theta = n\lambda$	'd' is inter-planar spacing, '2θ' is bragg's diffraction angle, 'n' is an integer, λ is the wavelength of X-ray.
Interplanar spacing	$d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$	(hkl) are miller indices of lattice plane, (a, b, c) are lattice parameters of the crystal.
Crystallite size, D (Schherrer equation)	$D = \frac{K.\lambda}{\omega \times \cos\theta}$	K is a constant, λ is the wavelength of X-ray, 'ω' is the FWHM, '2θ' is bragg's diffraction angle.
Specific capacitance, C_{sp} for single electrode (from CV)	$C_{sp} = \frac{\int IdV}{m \times \nu \times dV}$	'I' is the current, dV is the potential window, 'm' is the mass of active material, 'ν' is the scan rate.
Specific capacitance, C_{sp} for single electrode (from GCD)	$C_{sp} = \frac{2 \times I \times \Delta t}{m \times dV}$	'I' is the current, 'dt' is the discharging time, 'm' is the mass of active material.
Specific capacitance, C_{sp} for SSC/ASC (from GCD)	$C_{sp} = \frac{I \times \Delta t}{m \times dV}$	'I' is the current, 'dt' is the discharging time, 'm' is the mass of active material.
Energy density, E_d (from GCD)	$E_d = \frac{C_{sp} \times (dV)^2}{7.2}$	'C_{sp}' is the specific capacitance, dV is the voltage window.

Power density, P_d (from GCD)	$P_d = \frac{E_d \times 3.6}{\Delta t}$	'E_d' is the energy density, Δt is the discharging time.
Coulombic efficiency, η	$\eta = \frac{t_d \times 100}{t_c}$	't_d' is the discharging time and 't_d' is the charging time.
Response time, τ (from EIS)	$\tau = \frac{1}{\nu}$	'ν' is the frequency corresponding to phase angle $\theta = 45°$.

3. Results and Discussion

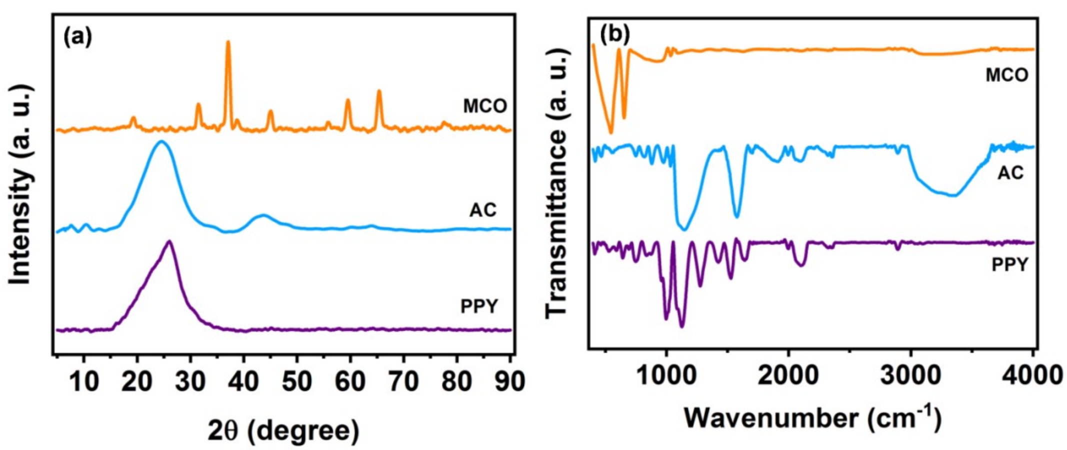

Fig. S1: (a) XRD and **(b)** FTIR patterns of MCO, AC, and PPY.

Table S2: XRD analysis for $MnCo_2O_4$ (MCO) microspheres.

Angle 2θ (degree)	**Lattice plane (hkl)**	**Interplanar spacing, d (Å)**	**Crystallite size (nm)**
19.3	(111)	4.6	9.1

31.5	(220)	2.8	11.2
37.1	(311)	2.4	11.1
38.7	(222)	2.3	11.9
45.3	(400)	2.0	11.4
55.5	(422)	1.6	14.2
59.5	(511)	1.5	10.7
65.3	(440)	1.4	10.6

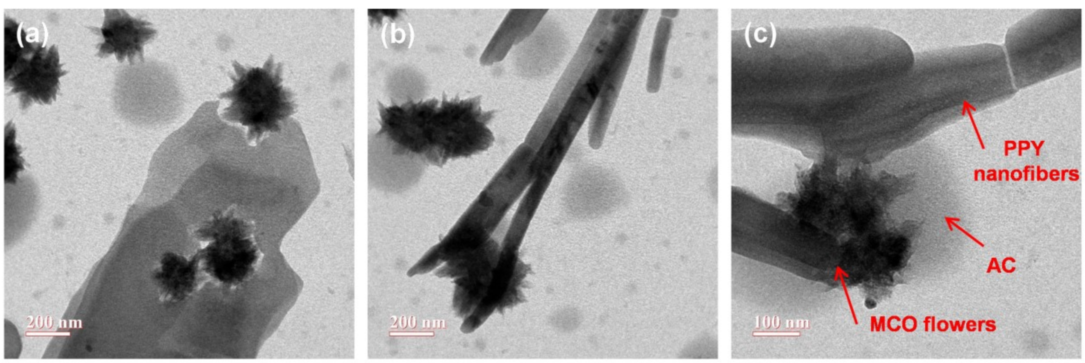

Fig. S2: (a-c) TEM images of MAP-20 at different resolutions.

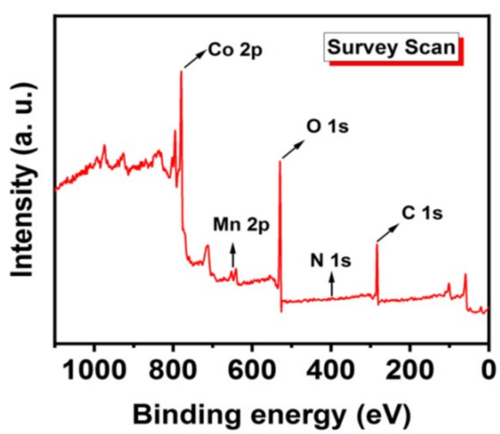

Fig. S3: XPS survey scan of MAP-20.

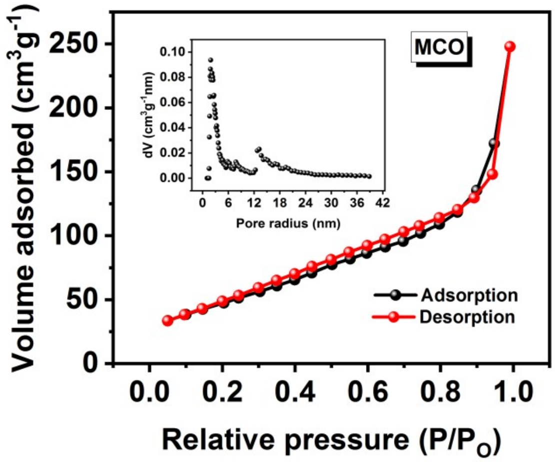

Fig. S4: BET analysis of pristine $MnCo_2O_4$ (MCO).

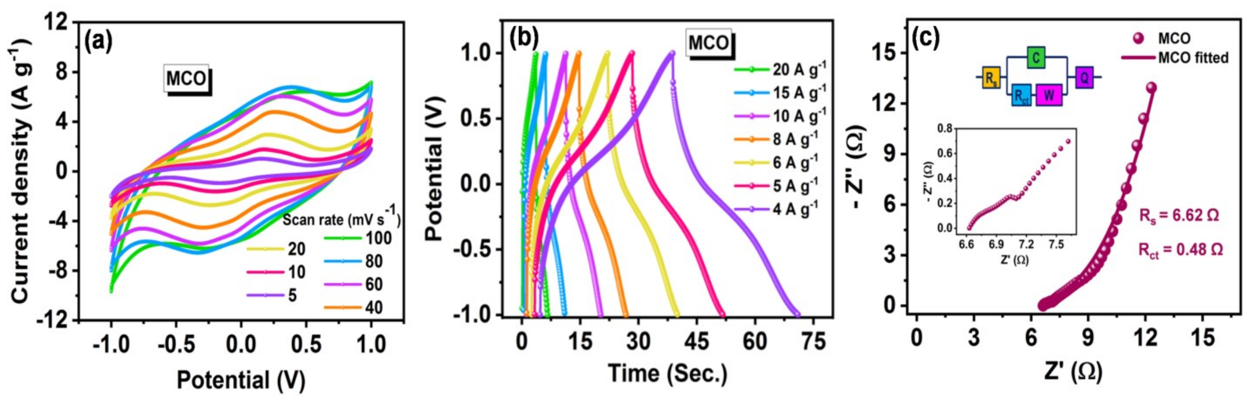

Fig. S5: (a) CV curves of MCO, **(b)** GCD curves of MCO and **(c)** Nyquist plot of MCO with fitted circuit.

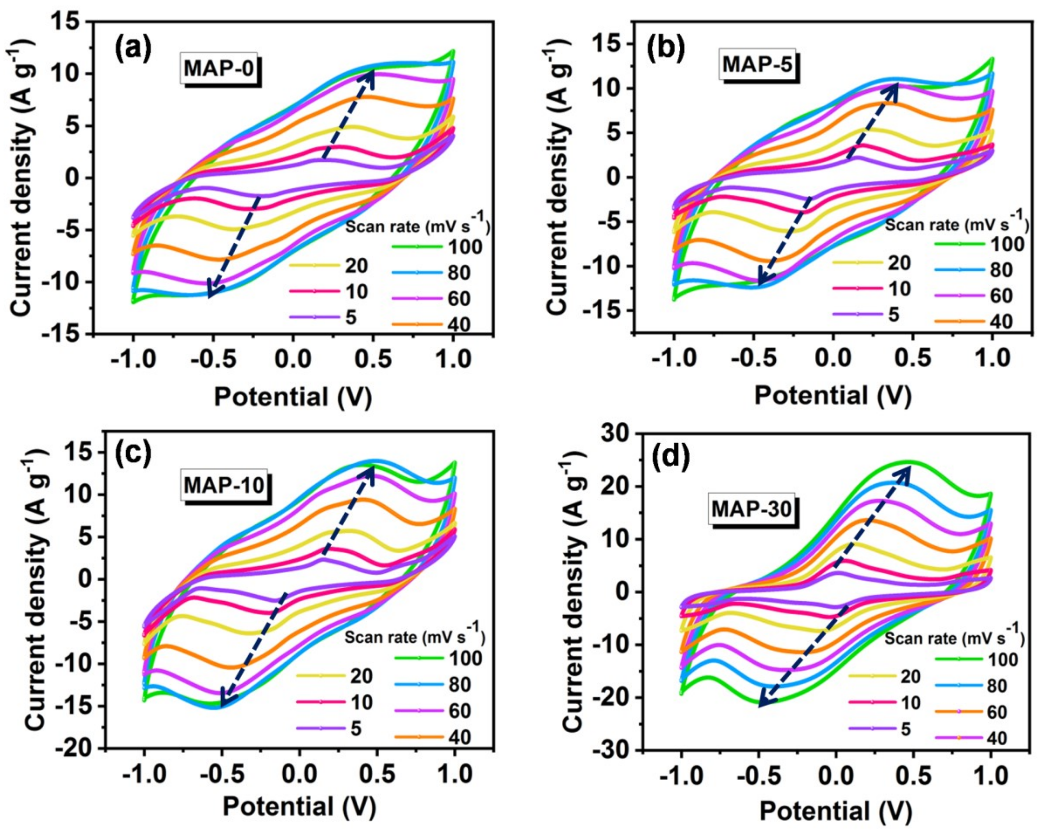

Fig. S6: (a-d) CV of MAP-x (x = 0, 5, 10, and 30) at various scan rates.

Power law

The power law gives the correlation of the current (i) and scan rates (v) as follows:

$$i = av^b \tag{S1}$$

where, a and b are adjustable constants.

Trasatti method

The total capacitance C_T of the electrode material is given by the combination of capacitance contribution of outer surface (C_o) and inner surface (C_i) and is given by the following formula:

$$C_T = C_o + C_i \tag{S2}$$

$$C = const. \times v^{-1/2} + C_o \tag{S3}$$

$$\frac{1}{C} = const. \times v^{1/2} + \frac{1}{C^T}$$

(S4)

where, C is the sp. capacitance calculated from the CV data.

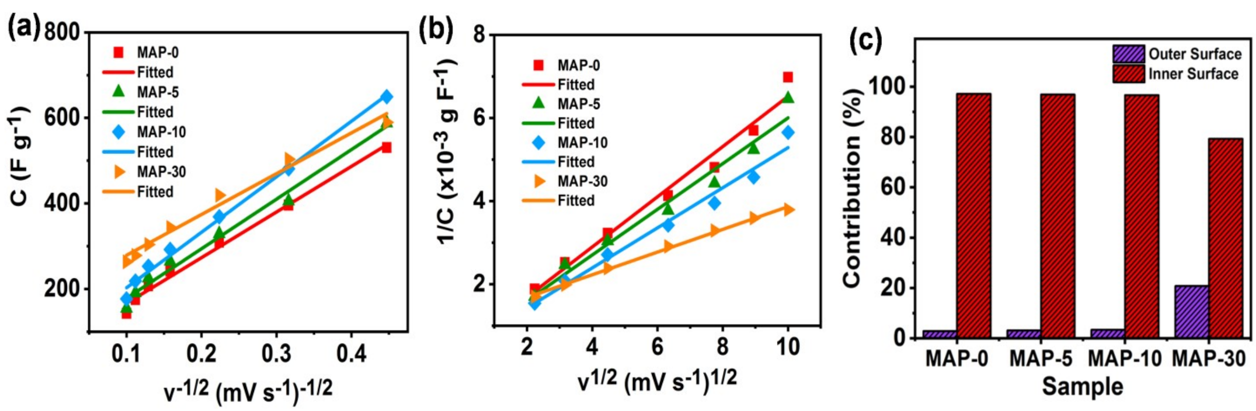

Fig. S7: (a-c) Charge storage kinetics of MAP-x (x = 0, 5, 10, and 30).

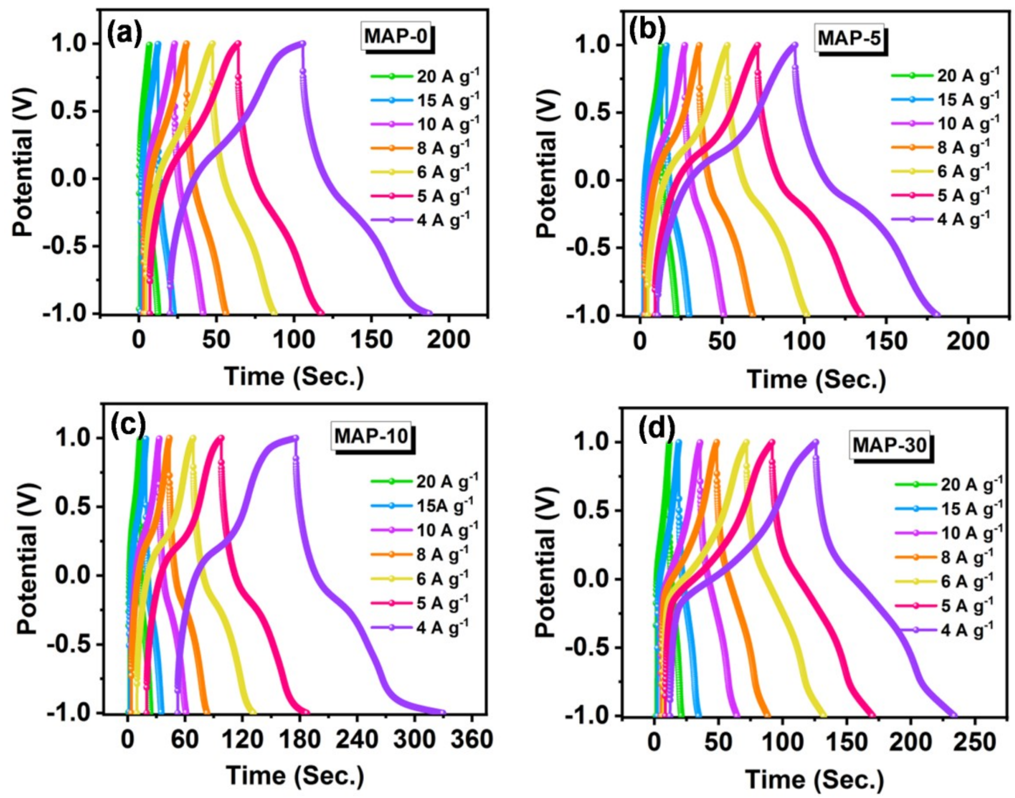

Fig. S8: (a-d) GCD of MAP-x (x = 0, 5, 10, and 30) at various scan rates.

Table S3: Comparison of supercapacitive performance of the prepared samples with literature.

Material	C_{sp} **(Fg^{-1})**	**Voltage window (V)**	**ASC/SSC**	**E_d (Wh kg^{-1})**	**Pd (kW kg^{-1})**	**Stability, % (cycles)**	**Reference**
$NiCo_2O_4$/NF@PPY	1717 C g^{-1}	0-1.6	ASC	68.9	1.77	89.2 (10,000)	[1]
$MnCo_2O_4$-graphite@PPY	2364	0-1.6	ASC	25.7	16.1	85.5 (10,000)	[2]
$NiCo_2O_4$@PPY	2244	0-1.6	ASC	58.8	0.36	89.2	[3]

	(1 A g^{-1})					(5,000)	
$NiCo_2O_4$/CNF@PPY	910 (1 A g^{-1})	0-1.5	ASC	40.8	0.73	88.0 (10,000)	[4]
$NiCo_2O_4/Co_3S_4$/MnS @PPY	2557 (1 A g^{-1})	0-1.6	ASC	81.1	0.80	83.6 (20,000)	[5]
$MgCo_2O_4$/PPY	988 (1 A g^{-1})	0-1.6	ASC	40.0	1.54	84.0 (10,000)	[6]
$MnNi_2O_4$/PPY	304 (1 A g^{-1})	0-1.6	ASC	35.9	0.80	--	[7]
CC@$NiCo_2O_4$@PPY	1687 (1 A g^{-1})	0-1.5	ASC	46.5	0.72	80.0 (10,000)	[8]
$NiCo_2O_4$@PANI	561 (10 mV s^{-1})	0-1.2	ASC	6.4	0.28	86.2 (3,000)	[9]
$ZnCo_2O_4$@PANI	720 (10 mV s^{-1})	0-0.5	--	--	--	96.4 (10,000)	[10]
$CuCo_2O_4$/GO@PANI	312.7 (1 A g^{-1})	0-1.2	SSC	62.5	5.99	84.2 (5,000)	[11]
$CoFe_2O_4$/PANI/GO	346.9 (1 A g^{-1})	0-1.2	SSC	69.3	5.98	79.0 (5,000)	[12]

Fe-$MnCo_2O_4$@PPY	422.4 (2 mA cm^{-2})	0-1	SSC	519.9 mWh cm^{-2}	--	94.7 (7,000)	[13]
$NiMoO_4$/rGO/PANI	1150 C g^{-1} (1 A g^{-1})	0-1.7	ASC	82.43	0.85	94.5 (10,000)	[14]
$NiCo_2O_4$/CF@PANI	369 mAh g^{-1}	0-1.5	ASC	60.6	2.32	--	[15]
$MnCo_2O_4$-AC@PPY	945.77 (5 mV s^{-1})	0-1.6	ASC	88.12	1.6	89.68 (10,000)	This work

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