Supporting Information

Mixed Solvent Exfoliated Transition Metal Oxides Nanosheets Based Flexible Solid State Supercapacitor Devices Endowed with High Energy Density

Shibsankar Dutta[a], Shreyasi Pal[b] and Sukanta De[a*]

[a]Department of Physics, Presidency University, 86/1 College Street, Kolkata-700073, India

[b]Department of Physics, Raidighi College, South 24 Parganas, Diamond Harbour Subdivision, Raidighi, West Bengal 743383, India

*Corresponding Author

E-mail: sukanta.physics@presiuniv.ac.in

Hansen solubility parameter (HSP) Study

The dissolution behavior can be explained by the Hansen solubility parameter (HSP) theory based on the three solubility parameters, these three dispersive (δ_D), polar (δ_P) and hydrogen bonding (δ_H) solubility parameters of solvent and solute are interrelated by the equation 1.

$$R_a = [4(\delta_{Dsolv} - \delta_{Dsolu})^2 + (\delta_{Psolv} - \delta_{Psolu})^2 + (\delta_{Hsolv} - \delta_{Hsolu})^2]^{\frac{1}{2}} \quad \textbf{(1)}$$

The solubility directly depends on the HSP distance (R_a) value, smaller R_a value provides us higher solubility.

Mixed solvent exfoliation can also be explained by Hansen theory where the each of three parameters is linear function of the volume fraction of the composition [equation 2]. [1]

$$\delta_{blend} = \sum \emptyset_{n,comp} \delta_{n,comp} \quad \textbf{(2)}$$

Where $\emptyset$ defines the volume fraction of each composition. Based on these two equations different solvent mixture can be predicted for the nano materials exfoliation.

HSP value for solvent and TMOs:

Solvent	δ_D (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)
Ethanol	15.8	8.8	19.4
Water	18.1	12.9	15.5
MoO_3	16.6	18.04	10.23
MnO_2	16.94	17.45	10.84
RuO_2	16.94	17.45	10.84

1. Supporting Figures

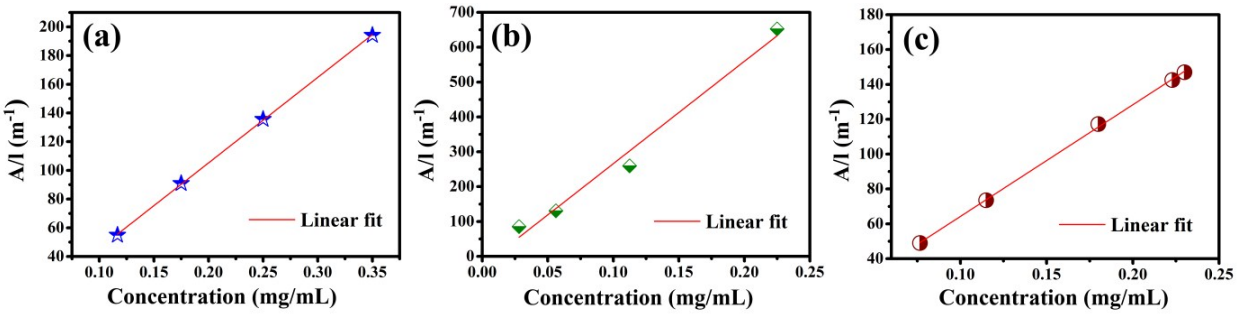

Figure S1† Absorbance per unit length (A/l) vs concentration (a) MoO_3, (b) MnO_2, (c) RuO_2.

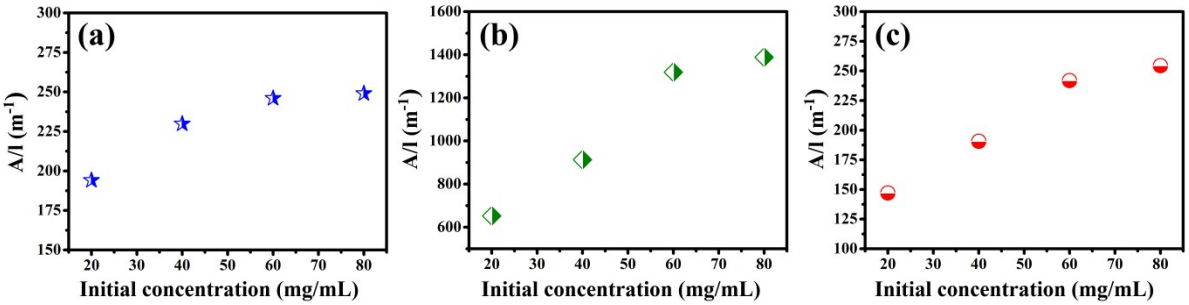

Figure S2† Absorbance per unit length (A/l) vs initial concentration (a) MoO_3, (b) MnO_2, (c) RuO_2.

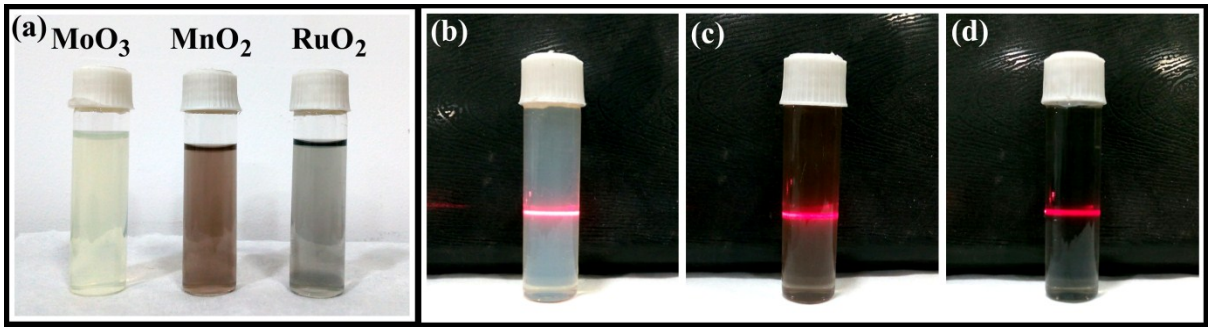

Figure S3† (a) Digital images of the MoO_3, MnO_2 and RuO_2 nanosheets dispersion in Ethanol/ water, (b-d) Tyndall effect of the exfoliated MoO_3, MnO_2 and RuO_2 nanosheets respectively.

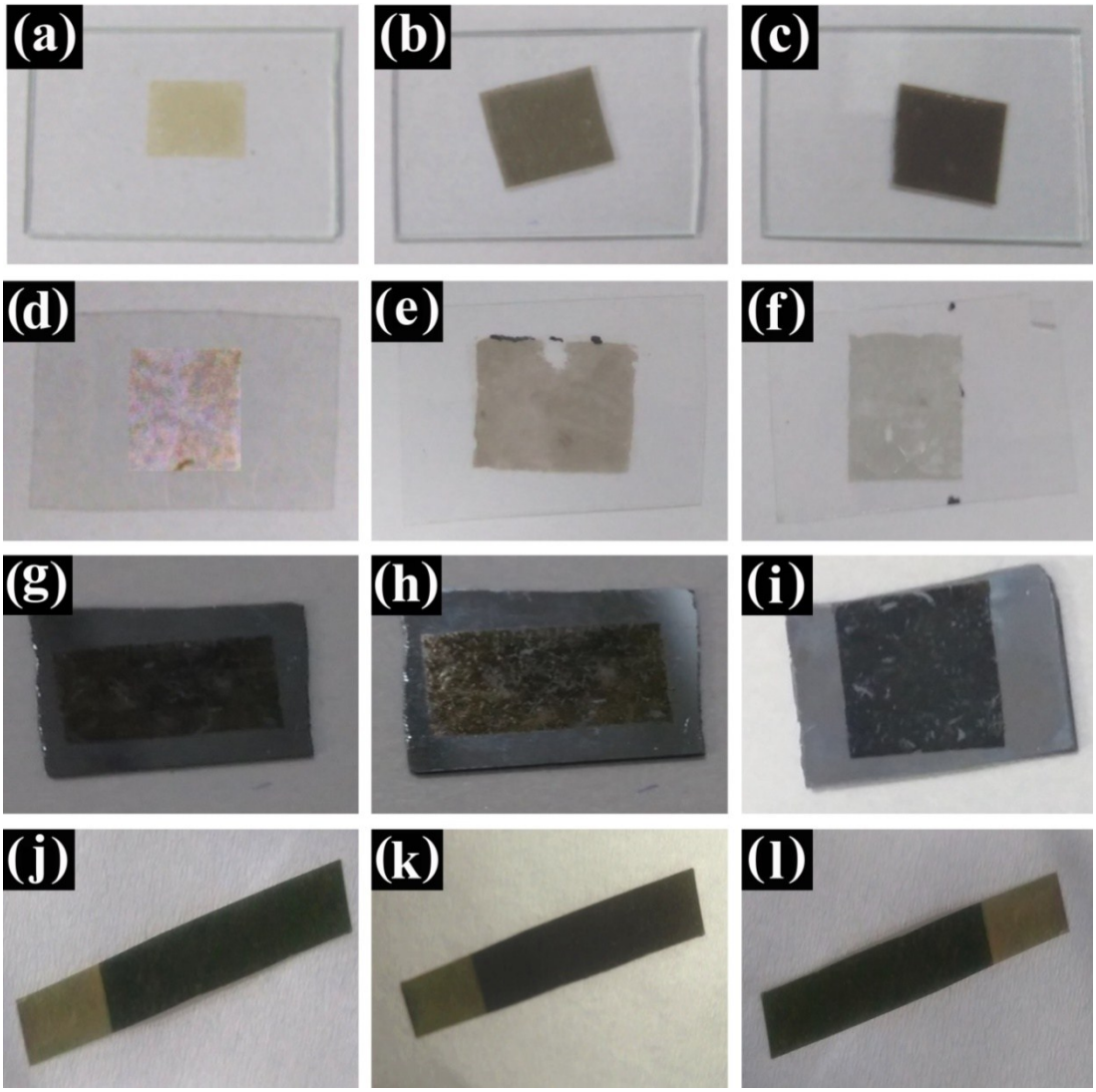

Figure S4† MoO_3, MnO_2 and RuO_2 nanosheets thin films on (a-c) glass, (d-f) PET substrate respectively. MoO_3/SWCNT, MnO_2/SWCNT and RuO_2/SWCNT nanocomposites thin films on (g-i) Si substrate and Au coated PET (j-l) substrate respectively.

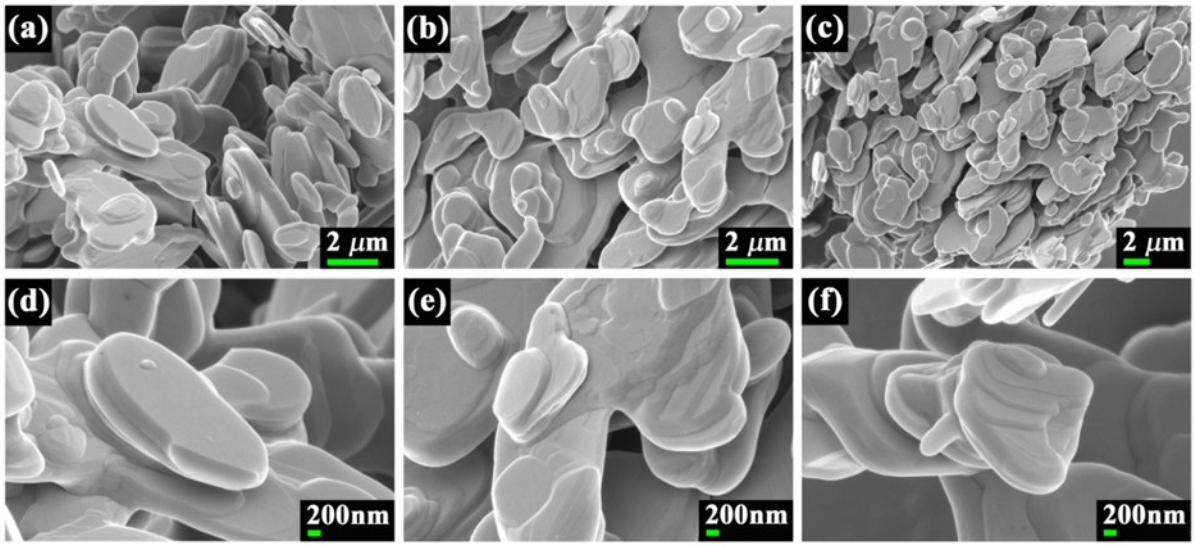

Figure S5† (a,b,c) FESEM images of the bulk MoO_3, MnO_2, RuO_2; (d,e,f) showing their high magnification FESEM images respectively.

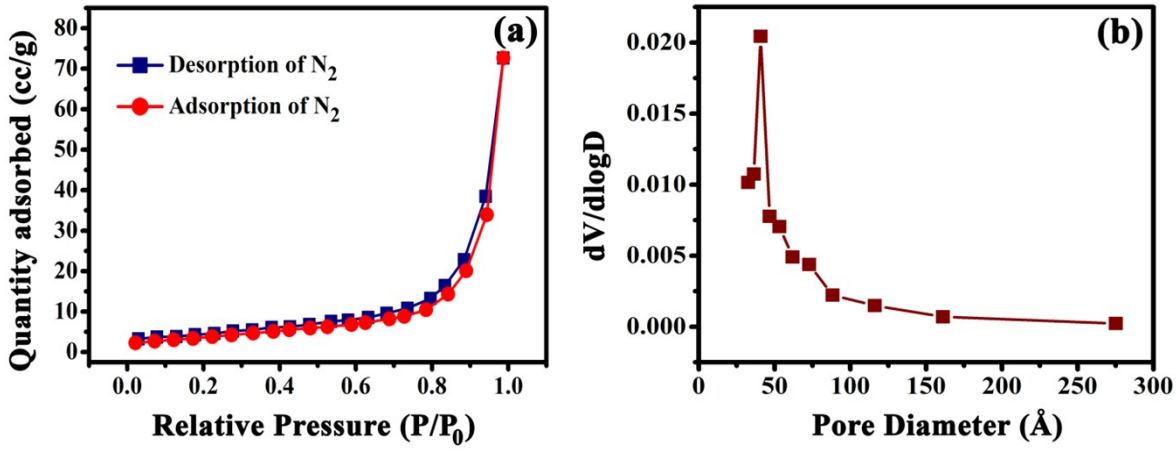

Figure S6† Nitrogen adsorption-desorption isotherm and corresponding pore size distribution curve of the pristine SWCNTs.

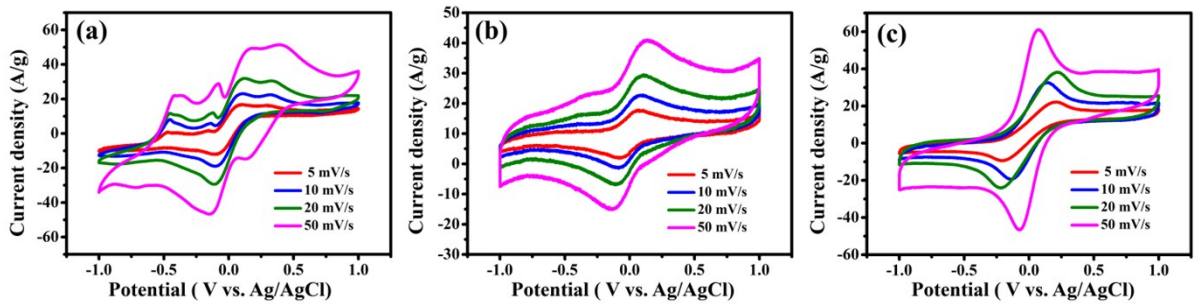

Figure S7† Cyclic voltrametry graph of (a) MoO_3/SWCNT,(b) MnO_2/SWCNT and (c) RuO_2/SWCNT at different scan rates respectively using three electrode system.

2. Specific capacitance calculations:

In the case of two electrodes solid state supercapacitor the specific capacitance value was calculated using equation (3) and (4), where m_2 was the total mass of the electrode materials, ν (V/s) is the scan rate and Δt (sec) is the discharge time.[2,3] Energy density (E) and power density (P) can also be calculated from the equations (5) and (6). [4]

$$C = \frac{4\int I_1\, dV}{\nu m_2 \Delta V} \text{.....(3)}$$

$$C = \frac{4I_2\, \Delta t}{m_2\, \Delta V} \text{.....(4)}$$

$$E = \frac{1}{8} C(\Delta V)^2 \text{.....} \quad (5)$$

$$P = \frac{1}{8} C\, \Delta V \nu \quad \text{.....(6)}$$

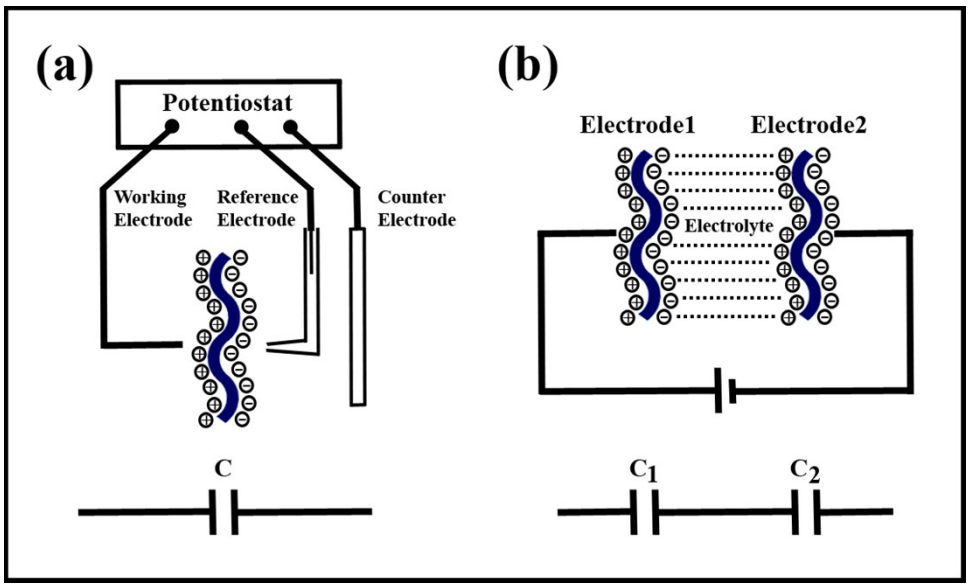

Figure S8† Schematic diagram and mechanism of the (a) three electrode and two electrode system.

Assuming the mass of the individual electrodes is m, the measured capacitance value for the two electrode system is:

$$c_{2E} = \frac{c}{2}$$ Where, $c_1=c_2=c$

Therefore the specific capacitance value is:

$$c_{specific-2E} = \frac{c_{2E}}{2m} = \frac{c}{4m}$$

In the case of three electrode system:

$$c_{3E} = c$$

Therefore the specific capacitance value is

$$c_{specific-3E} = \frac{c_{3E}}{m} = \frac{c}{m}$$

The relation between the calculated specific capacitance value in the two and three electrode system is

$$c_{specific-3E} = 4 \times c_{specific-2E}$$

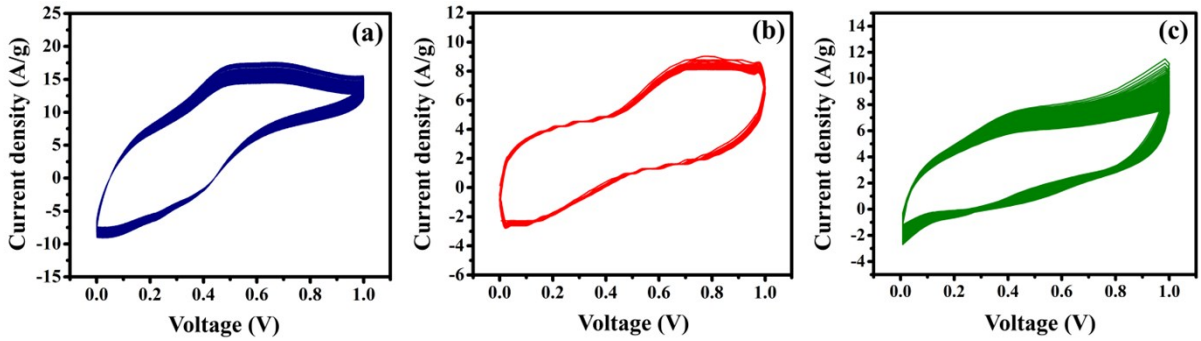

Figure S9† Cyclic voltrametry graph of (a) MoO_3/SWCNT,(b) MnO_2/SWCNT and (c) RuO_2/SWCNT at 100 mV/s scan rates for 1000 cycles respectively using two electrode system.

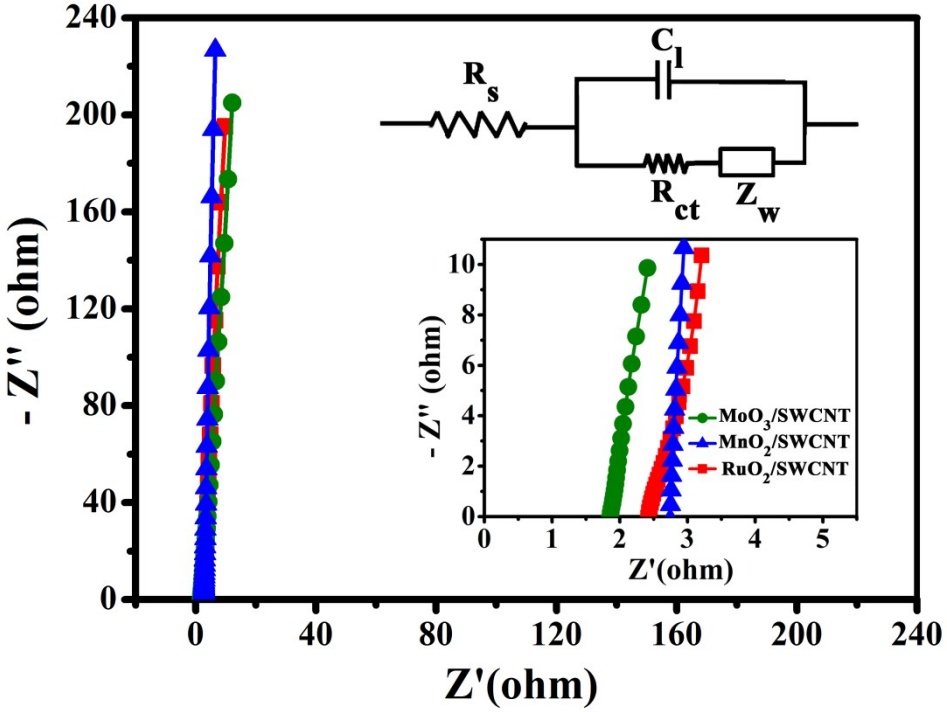

Figure S10† Nyquist plot of the all solid state supercapacitors; Inset showing the enlarge view of high frequency region and an equivalent circuit model.

3. The electrochemical behavior and charge discharge mechanism of the TMOs

According to the charge-storage mechanism the electrochemical reaction occurring at MoO_3/SWCNT electrode is

$$2MoO_3 + 2H^+ + 2e^- \leftrightarrow Mo_2O_5 \text{.....(7)}$$

The charge-storage mechanism of MnO_2/SWCNT electrode involves a reversible reduction/oxidation between Mn^{4+} and Mn^{3+}, which can be denoted as Eq. (8)

$$MnO_2 + H^+ + e^- \leftrightarrow MnOOH \text{.....(8)}$$

And the charge discharge mechanism of the RuO_2 can be explain by the reversible reactions given below

$$RuO_2 + \beta H^+ + \beta e \leftrightarrow RuO_{2-\beta}(OH)\beta \text{.....(9)}$$

Table S1. Comparison of the electrochemical performance of the TMOs/SWCNT supercapacitor with previously reported metal oxide supercapacitors.

Electrode materials	Electrolyte	Specific capitance (F/g)	Energy density (Wh kg^{-1})	Power density (kW kg^{-1})	Ref.
graphene/MnO_2 // graphene/Ag	-	-	7.53	90.3	5
3D Al@Ni@ MnOx nanospike// CCG	Na_2SO_4/PVA	-	23.02	0.947	6
MnO_2@PANI// 3D graphene foam (GF	KOH/PVA	95.3	37	0.386	7
Waste paper fibersRGO–MnO_2	PVA/Na_2SO_4	220	19.6	2.4	8
MnO_2 nanoflakes	PVP/$LiClO_4$	-	23	1.9	9
SWCNTs//RuO_2	PVA/H_3PO_4	138	18.8	96	10
Graphene(IL-CMG)//RuO2-IL-CMG	PVA–H_2SO_4	175	19.7	6.8	11
MnO_2 //Mesoporous CNT	Na_2SO_4	85.8	47.4	0.200	12
Graphene/MnO_2 //Graphene	Na_2SO_4	31.0	30.4	0.100	13
Graphene/MnO_2 //ACF	Na_2SO_4	113.5	51.1	0.198	14
Activated graphene/MO_2 //Activated graphene	Na_2SO_4	175	32.3	21	15
Graphene/PANi//Graphene/ RuO_2	KOH	-	26.3	0.150	16
TiO_2 //CNT	$LiPF_6$	-	12.5	0.300	17
Graphene/$Ni(OH)_2$ //Graphene/RuO_2	KOH	-	48.0	0.230	18
Carbon spheres/MnO_2 //Carbon spheres	Na_2SO_4	-	22.1	0.100	19
CNT/MnO_2 //CNT/In_2O_3	Na_2SO_4	-	25.0	-	20
Graphene/MnO_2 //Graphene/MoO_3	Na_2SO_4	307	42.6	0.276	21
MoO_3/SWCNT// MoO_3/SWCNT	PVA/H_2SO_4	717	24.89	1.61	Present Work
	1 M Na_2SO_4 (Three electrode)	1205.08	669	21.69	
MnO_2/SWCNT// MnO_2/SWCNT	PVA/H_2SO_4	540	18.73	1.21	
	1 M Na_2SO_4 (Three electrode)	1168.69	649.27	21.03	
RuO_2/SWCNT// RuO_2/SWCNT	PVA/H_2SO_4	676	23.48	1.52	
	1 M Na_2SO_4 (Three electrode)	1308.45	726.91	23.55	

Reference

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