Electronic Supplementary Information

Hierarchical Three-Dimensional Mesoporous MnO_2 Nanostructure for High Performance Aqueous Asymmetric Supercapacitor

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Asymetric supercapacitor electrodes

The mass ratio of the two electrodes in the asymmetric supercapacitor was calculated by following the charge balance of the electrode. The specific capacitance of the rGO from charge-discharge was calculated to be 122 F/g at a current density of 1 A/g.

To maintain the equal charge balance in both the electrode,

$$Q_+ = Q_-$$

$$m_+ \times Cs_+ \times \Delta E_+ = m_- \times Cs_- \times \Delta E_-$$

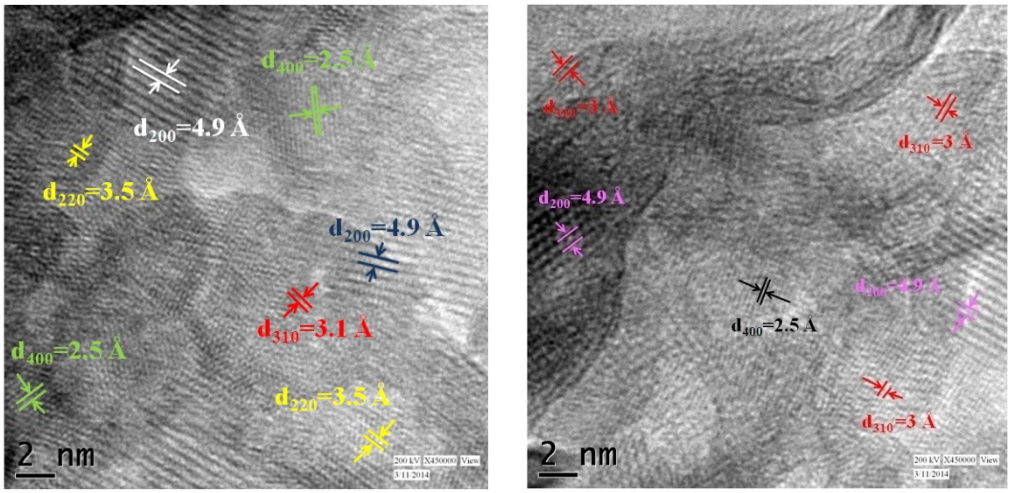
$$\frac{m_-}{m_+} = \frac{Cs_+ \times \Delta E_+}{Cs_- \times \Delta E_-}$$

$$\frac{m_-}{m_+} = \frac{322 \times 1}{122 \times 1} = 2.63$$

The mass ratio of the rGO and α-MnO_2 electrode is 2.63 in the ASC. The mass of the cathode electrode material (α-MnO_2) was kept ~0.8 mg. rGO (2.1 mg) was used in the anode for the ASC fabrication.

ESI 1

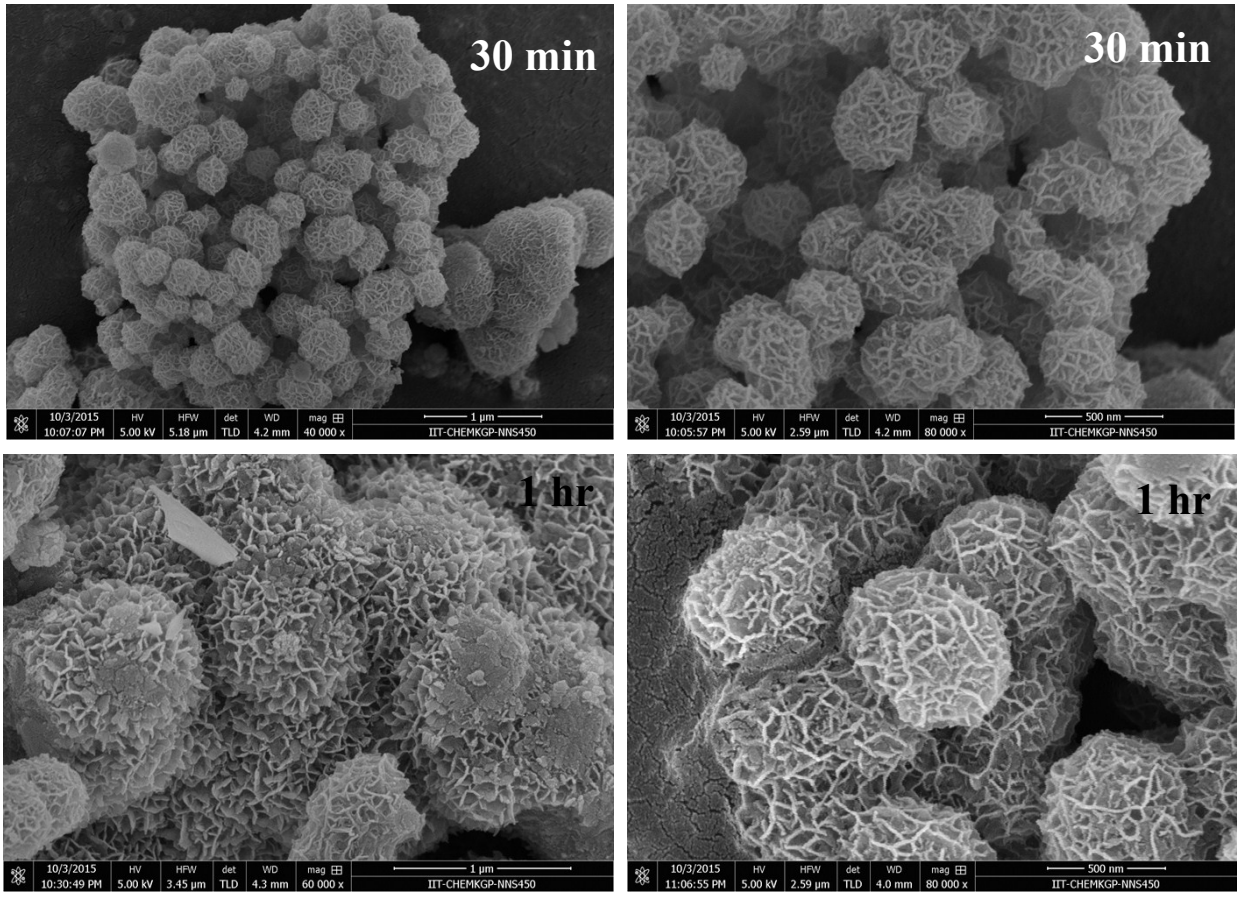
HRTEM images of the mesoporous α-MnO_2 nanostructure.



The lattice spacing of 4.9 Å, 3.5 Å, 3.1 Å, 2.5 Å in the HRTEM images corresponds to the (200), (220), (310), and (400) planes of α-MnO_2. These planes are also observed in the XRD profile of the mesoporous α-MnO_2 (Figure 3).

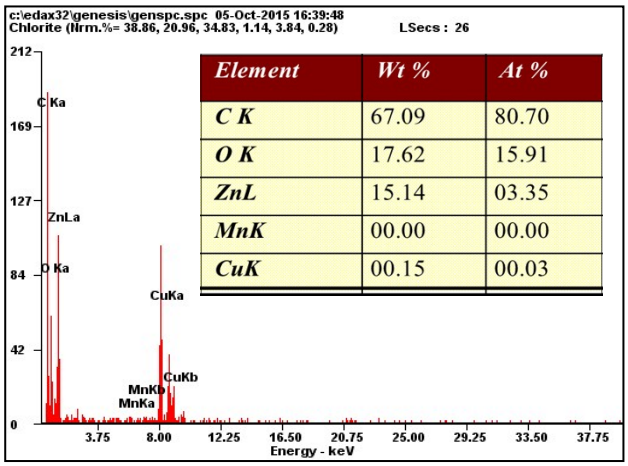
ESI 2

FESEM image of the MnO_2 nanostruture after 30 min and 1 hr of the reaction.



ESI 3

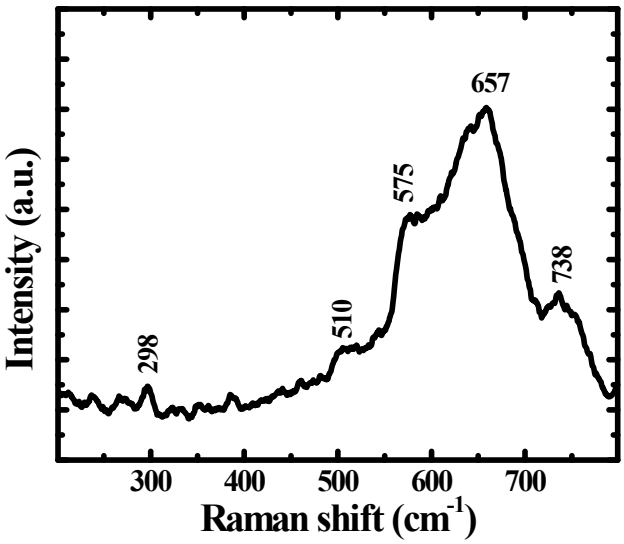
EDS profile of the sample (obtained at 15 min) corresponding to Figure 2(a-c).



Element	Wt %	At %
C K	67.09	80.70
O K	17.62	15.91
ZnL	15.14	03.35
MnK	00.00	00.00
CuK	00.15	00.03

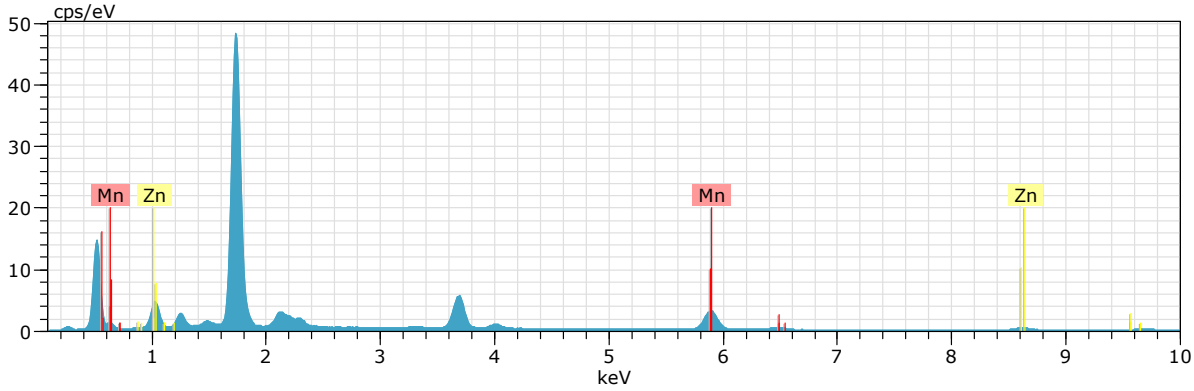
ESI 4

Raman spectral profile of α-MnO_2.



ESI-5

Energy dispersive X-ray spectroscopic (EDS) profile of mesoporous α-MnO_2 nanostructure.

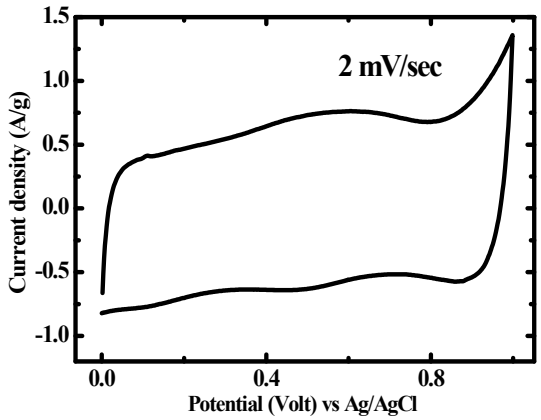


Spectrum: Objects 55

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Mn	25	K-series	28.42	50.67	28.53	0.78
O	8	K-series	19.26	36.77	68.75	2.27
Au	79	L-series	6.24	10.91	1.73	0.22
Zn	**30**	**K-series**	**1.51**	**1.64**	**0.98**	**0.07**
		Total:	57.22	100.00	100.00	

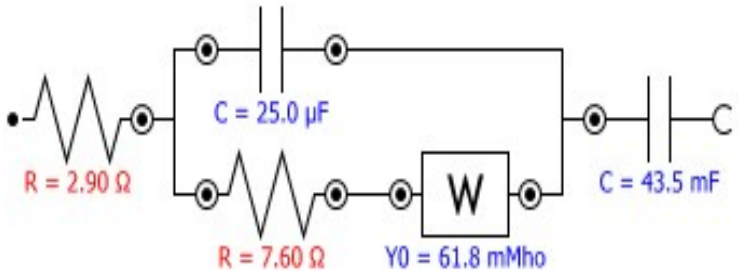
ESI 6

Cyclic voltammogram of mesoporous α-MnO_2 electrode in 1 M Na_2SO_4 at a scan rate of 2 mV/sec.



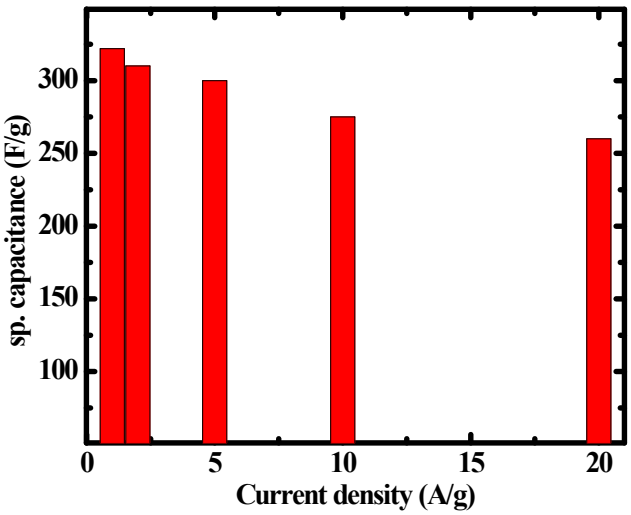
ESI 7

Equivalent circuit used to fit the Nyquist plot shown in Figure 6c.



ESI 8

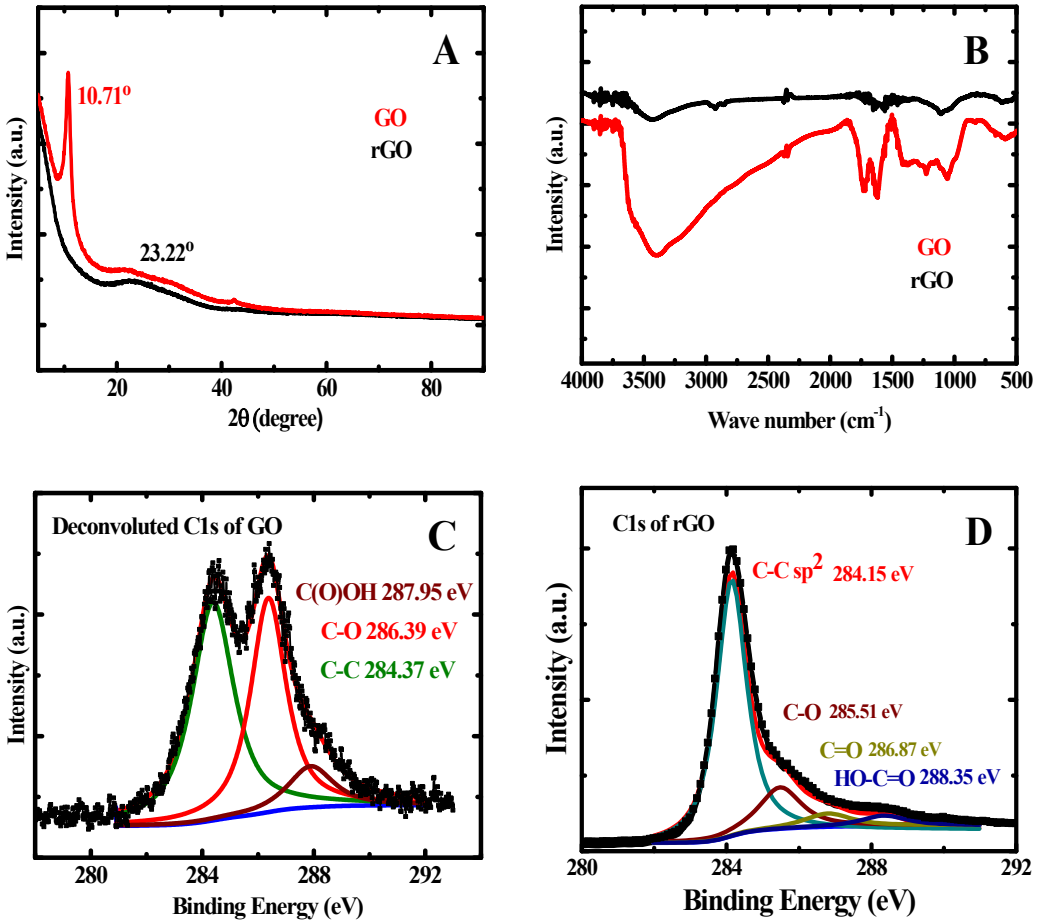
Plot illustrating the rate capability of the mesoporous α-MnO_2 electrode at different current densities.



The specific capacitance was calculated from charge-discharge experiments at different current densities. The electrode has >80% rate capability even at 20 A/g as shown in the above figure.

ESI 9

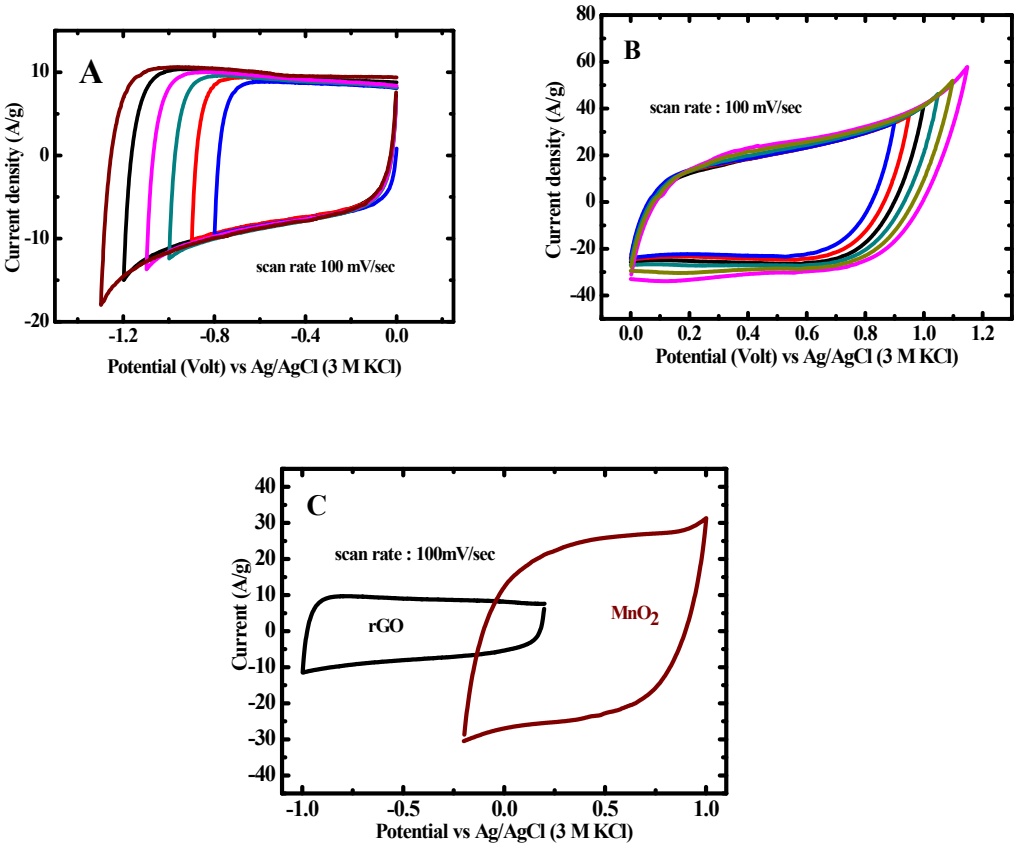
XRD pattern (A), FTIR spectra (B) and deconvoluted C1s XPS spectra of GO (C) and rGO (D).



The XRD profile and FTIR spectrum of GO and rGO in the ESI 9A,B confirm the reduction of GO. The deconvoluted C1s spectrum of rGO in the ESI 9D also reveals the successful removal of the oxygen containing functionalities in GO (ESI 9C).

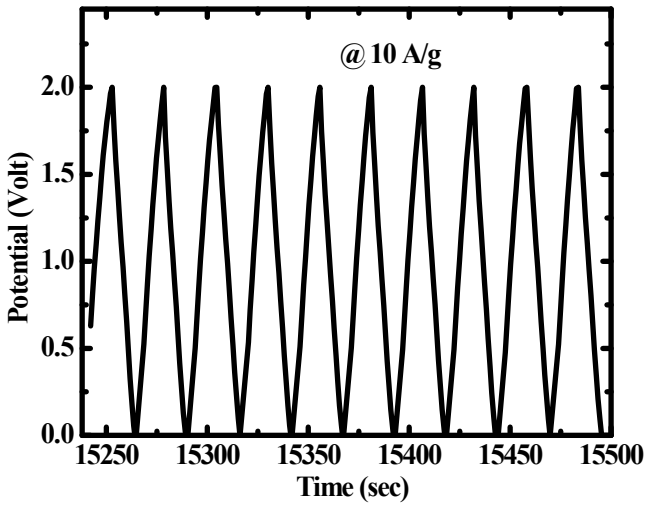
ESI 10

Cyclic voltammogram obtained for rGO anode (A) and mesoporous α-MnO_2 cathode (B) in 1 M Na_2SO_4 at a scan rate of 100 mV/sec at different potential windows. The comparative voltammograms of the anode and cathode is shown in (C). All the voltammograms were acquired with three electrode electrochemical cell.



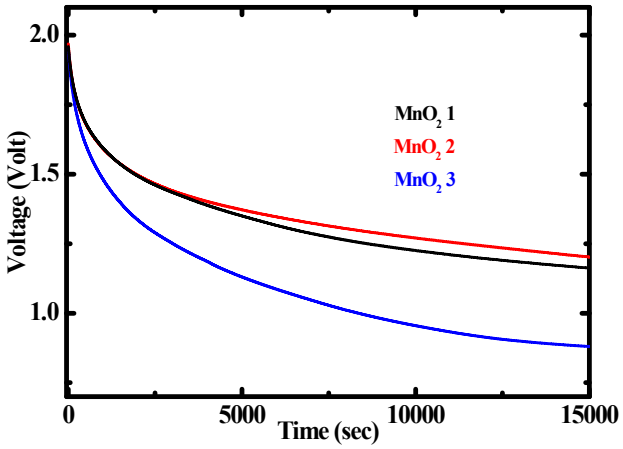
ESI-11

The repeated charge-discharge cycle of the asymmetric supercapacitor device, made by pairing of mesoporous MnO_2 and rGO electrode at a constant current density of 10 A g^{-1}.



ESI 12

Self-discharge profile of Asymmetric supercapacitor Devices made of three different amout of Zn containg α-MnO_2.



The ASC was charged at the current density of 1A/g for 5 minutes to completely charge. The self discharge profile was obtained at the open circuit potential of 2 V at room temperature. The self-discharge mechanism could be associated with the trace impurity present along with the electrode material (Electrochemical supercapacitor, B.E. Conway, electrochemical supercapacitor for energy delivery and storage, A.Yu, V. Chabot, J. Zhang).

Table S1

Summary of literature on synthesis of porous MnO_2.

Reference	Synthetic procedure	Surface area BET (m^2g^{-1})
Inorg. Chem. 2006, **45**, 6404-6410	**80 °C 6 h** using Cu and $KMnO_4$	132
J. Phys. Chem. C 2007, **111**, 19141-19147	**Hydrothermal** treatment of $KMnO_4$ and H_2SO_4 solution for **12 hrs at 110°C.**	108.6
Nanotechnolgy 2008, **19**, 185604-185611	Sol-gel method and followed by **calcination**	142.6
J. Phys. Chem. C 2008, **112**, 7270-7277	oxidation of the pyrochroite $Mn(OH)_2$ by potassium persulfate $K_2S_2O_8$ and addition of NaOH	20
J. Phys. Chem. C 2009, **113**, 14020–14027	$MnSO_4$ solution was mixed with $K_2S_2O_8$ solution. NaOH solution was added dropwise, and dried for **24 hr**.	135
Cryst. Growth Des. 2009, **9**, 528	Hydrothermal method, $K_2S_2O_8$ and $MnSO_4$ in presence of sulfuirc acid, **110 °C 6 h**	-
J. Phys. Chem. C 2010, **114**, 2694–2700	**Using SBA-15 as a template**, $Mn(NO_3)_2$ solution was irradiated with ultrasound followed by **annealing**	266
Electrochim. Acta 2010, **55**, 5117–5122	$KMnO_4$ was reacted with CNTs or mesoporous carbon for **12 hr at 120°C**	81
J. Phys. Chem. C 2011, **115**, 5413–5421	$KMnO_4$ was mixed with ascorbic acid and then calcined	222
Electrochem. Solid State Lett., 2012, **15**, A57-A59	**CTAB was used as a soft template** and $KMnO_4$ was reacted with $Mn(OOCCH_3)_2$	178
Cryst. Eng. Comm., 2012, **14**, 4196	Hydrothermal, $KMnO_4$ **150-200 °C, 24 h**	8.511
ACS Appl. Mater. Interfaces 2012, **4**, 2769−2774	Different nanostructures using **carbon template and hydrothermal approach at high temperature**	90
J. Power Sources 2013, **243**, 676-681	Electrodeposition on Ni foam	-
ACS Appl. Mater. Interfaces 2014, **6**, 9776 −9784	$MnSO_4$ and $KMnO_4$ was mixed in CH_2Cl_2/H_2O and kept for **2 days** and then dried and calcined.	219.3
J. Power Sources 2014, **270**, 411	$KMnO_4$, mannitol, **80 °C**	199
J. Power Sources 2015, **280**, 526-532	$KMnO_4$ and $MnSO_4$ in Teflon lined autoclave for **14 hr at 140°C**	93.4
J. Power Sources 2015, **277**, 36-43.	Ni foam template and $KMnO_4$ solution was sealed the autoclave and maintained at **160 °C** *for* **24 h**	236.8
This work	**Room temperature reduction of $KMnO_4$ by Zn within 2 h**	206

Table S2

Specific capacitance and conductivity dependence on the amount of Zn and Zn(II) ions on MnO_2.

Three types of MnO_2 samples were prepared using three different amount of metallic Zinc powder and the amount of Zinc was measured by EDAX.

The conductivity and sheet resistance were obtained from the resistivity by using the following equation:

Conductivity (σ) = 1/ Resistivity (ρ)

Sheet resstance (Rs) = Resistivity (ρ)/ thickness of film (t)

Sample	**Atomic % of Zn**	**Resistivity (ohmcm)**	**Conductivity (S/cm)**	**Sheet resistance (kohm/□)**	**Specific capacitance (Fg^{-1})****	**Cycle performance** #
MnO_2 1	0.42	8.95×10^3	1.12×10^{-4}	2.13	254	87% after 8000 cycles
MnO_2 2	0.98	1.37×10^3	7.29×10^{-4}	0.65	322	90 % after 8000 cycles
MnO_2 3	1.85	1.13×10^3	8.85×10^{-4}	0.51	311	88% after 8000 cycles

** current density = 1 A/g (obtained with three-electrode system)

current density = 20 A/g

Table S3

Electrochemical performances of the recent report on mesoporous/porous MnO_2 nanostructure towards supercapacitor electrode material.

Reference	Specific capacitance	Electrolyte	Rate capability	Cycle performance
Cryst Growth Des, 2009, **9**, 528–533	120 F g^{-1} at 5 mVs^{-1}	1 M Na_2SO_4	75% at 200mVs^{-1}	-
Electrochim. Acta 2010, **55**, 5117–5122	232 Fg^{-1} at 5 $mAcm^{-2}$	1M Na_2SO_4	87.4% at 10 mA/cm^2	92.6% after 500 cycle @ 5 mA/cm^2
J. Phys. Chem. C 2011, **115**, 5413–5421	200 Fg^{-1} at 6.0 mA cm^{-2}	0.5M Na_2SO_4	-	-
ACS Appl. Mater. Interfaces 2012, **4**, 2801−2810	266.8 Fg-1 at 1 A/g	1 M Na_2SO_4	62% at 10Ag-1	-
ACS Appl. Mater. Interfaces 2012, **4**, 2769−2774	461 Fg^{-1} at 5 mV/s	1 M Na_2SO_4	53.79% at 100mV/s	~99.99% after 3000 cycle @ 5 Ag^{-1}
Nanoscale, 2012, **4**, 807	218 F g^{-1} at 0.1 A g^{-1}	1 M Na_2SO_4	-	-
Electrochem. Solid State Lett., 2012, **15**, A57-A59	297 F g−1	0.1 M Mg(ClO4)2.	-	95 % after 200 cycles @ 0.5 mA
J. Power Sources 2013, **243**, 676-681	201 F/g at 1 A/g	1 M Na_2SO_4	48% at 20 Ag^{-1}	65% after 1800 cycles @ 5Ag^{-1}
Sci. Rep. 2014, **4**, 3878;	365 F g^{-1} at 0.25 Ag^{-1}	1 M Na_2SO_4	55.53% at 10 Ag^{-1}	90.4% after 3000 cycle @ 5Ag^{-1}
Nano Energy 2014, **4**, 39–48	292 F/g at 2.5 A/g	1 M Na_2SO_4	49% at 8 A/g	76% after 3000 cycle at 5A/g
ACS Appl. Mater. Interfaces 2014, **6**, 17637−17646	309 F/g, 5 mV/s	1 M Na_2SO_4	16% at 100mV/s	~25% after 5000 cycles @ 5 A/g
J. Power Sources 2014, **270**, 411-417	180 F g^{-1} at 2mV/s	1 M Na_2SO_4	~65% at 50mV/sec	~99% after 10, 000 cycle @ 10mVs^{-1}
This work	322 Fg^{-1} at 1 Ag^{-1}	1 M Na_2SO_4	80% at 20 Ag^{-1}	> 90% after 8000 cycle @ 20 A/g

Table S4

Table summarizing the energy and power density of the MnO_2 based asymmetric supercapacitor device.

Article	Supercapacitor device details	Energy density	Power density
Appl. Phys. A, 2006, **82**, 599–606.	Activated carbon/MnO_2 device in K_2SO_4	15Wh/kg	1.2 kW/kg
J. Phys. Chem. C 2009, **113**, 14020–14027.	MnO_2//Activated carbon in Li_2SO_4	28.4 Wh/kg,	0.15 kW/kg
J. Power Sources 2009, **194**, 1222–1225	$NaMnO_2$//Ac in 0.5 M Na_2SO_4	19.5Whkg^{-1}	130Wkg^{-1}
ACS Nano 2010, **4**, 5835–5842.	Graphene MnO_2//Graphene in 1M Na_2SO_4	7.0 Wh kg^{-1}	5.0kW kg^{-1}
J. Power Sources 2010, **195**, 2789–2794	$K_{0.27}MnO_2 \cdot 0.6H_2O$//AC in 0.5 M K_2SO_4	25.3Whkg^{-1}	140Wkg^{-1}
ACS Nano 2010, **4**, 4403–4411.	MnO_2//CNT flexible solid device	25.5 Wh/kg	-
Nano Lett., 2011, **11**, 2905–2911.	GrapheneMnO_2//SWNT in 0.5 M Na_2SO_4	12.5Wh/kg	-
Adv. Funct. Mater. 2011, **21**, 2366–2375.	Graphene/MnO_2 //CAN in 1 M Na_2SO_4	51.1 Wh kg^{-1}	0.1022 kW kg^{-1}
Nanoscale 2012, **4**, 807–812.	MnO_2 nanoflowers //Functional mesoporous CNTs in 1M Na_2SO_4	47.4Wh kg^{-1}	0.2 kWkg^{-1}
ACS Appl. Mater. Interfaces 2012, **4**, 2801−2810.	MnO_2// graphene hydrogel, in K_2SO_4	23.2 Wh kg^{-1}	1.0 kW kg^{-1}.
ACS Nano 2012, **6**, 4020–4028.	MnO_2/e-CMG film// Graphene in 1M Na_2SO_4	44 Wh/kg	11.2 kW/kg
J. Mater. Chem. C, 2013, **1**, 1245–1251.	Graphene/MnO_2//graphene/Ag asymmetric.	50.8 W h kg^{-1}	0.101kW Kg^{-1}
Nano Lett. 2013, **13**, 2151−2157.	MnO_2//rGO hybrid planar flexible solid device	17 Wh/kg	2.52 kW/kg,
Adv. Mater. 2013, **25**, 4746–4752.	Bacterial cellulose (BC) - MnO_2 //BC in 1 M Na_2SO_4	32.91 W h kg^{-1}	284.63 kW kg^{-1}
This work	MnO_2//reduced graphene oxide in 1M Na_2SO_4	35.28Wh/kg	2 kWh/kg