Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Facile Shape-Controlled Growth of Hierarchical Mesoporous δ-MnO_2 for the Development of Asymmetric Supercapacitor

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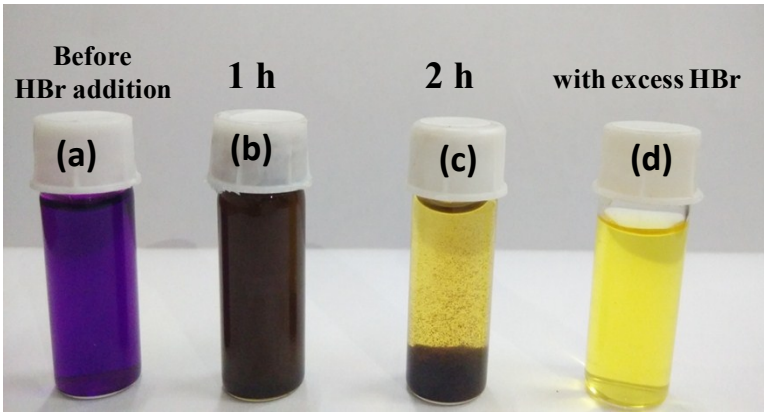
Figure S1

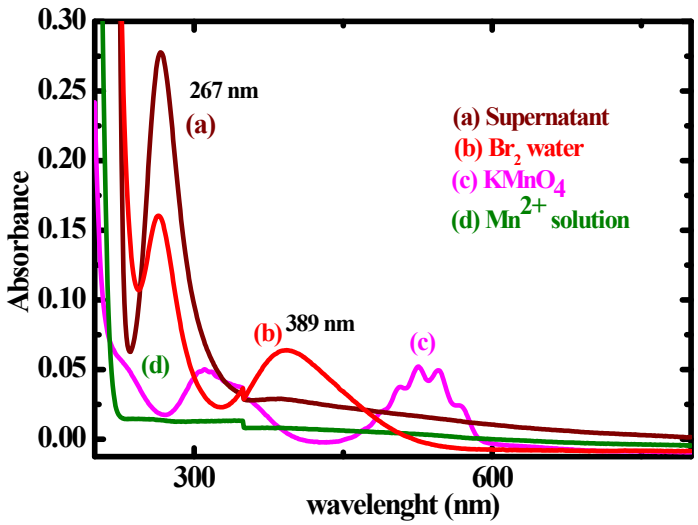
Digital images acquired at different time interval of the reaction between HBr and $KMnO_4$ (molar ratio 5:1). (a) Before the addition of HBr, (b,c) after the addition: at 1 (b) and 2 h (c) of the reaction. (d) Digital image of the reaction mixture (10:1 molar ratio) after 2 h of the reaction.



The digital image of the reaction mixture after 2 h shows the completion of the reaction. The yellow color of the supernatant is due to the Br_2 evolution due to oxidation of Br^-. In presence of excess Br^- the as-produced MnO_2 is completely reduced to Mn^{2+}.

Figure S2

UV-vis spectra of (a) $KMnO_4$ solution, (b) Br_2 water, (c) Mn^{2+} in water and (d) supernatant solution obtained after the reaction in 5:1 molar ratio.



The UV-vis spectrum of supernatant shows negative test for MnO_4^-, suggesting complete reaction of $KMnO_4$ with HBr; the supernatant after completion of the reaction exhibit two peaks at 267 and 389 nm corresponding to Br_2 in water.

Figure S3

TEM (A, B) and HRTEM (C) images of MnO_2 obtained at 1:1 molar ratio of $KMnO_4$ and HBr.

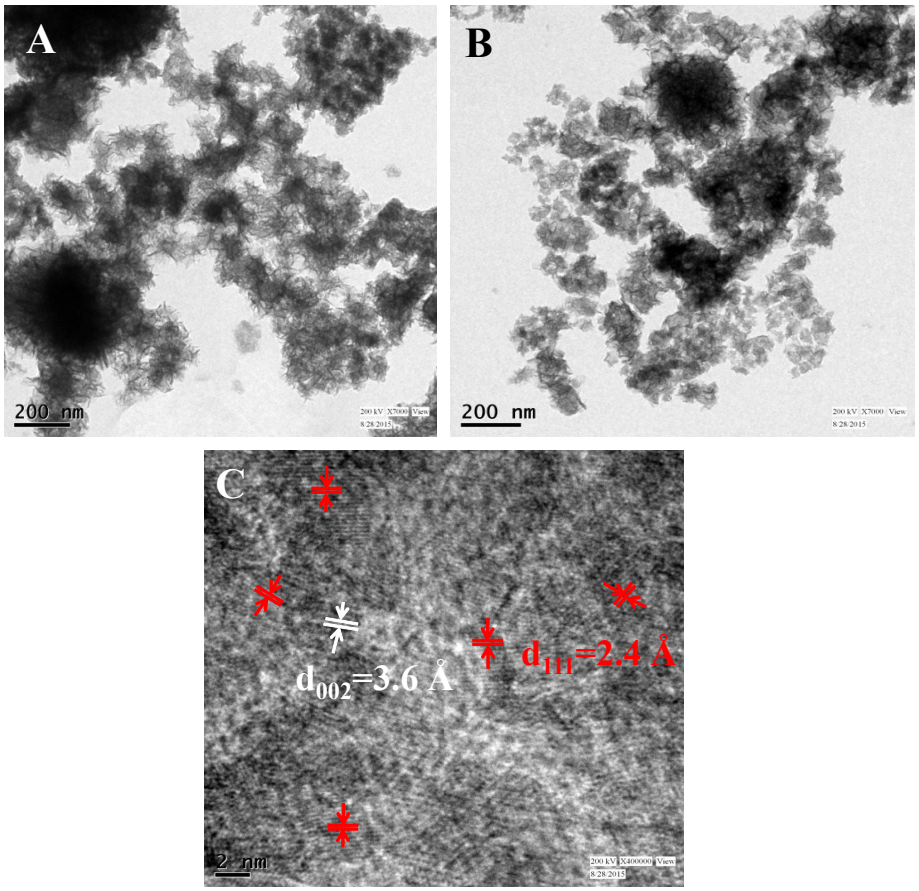


Figure S4

TEM (A, B) and HRTEM (C) images of MnO_2 obtained at the molar ratio of 3:1 HBr and $KMnO_4$.

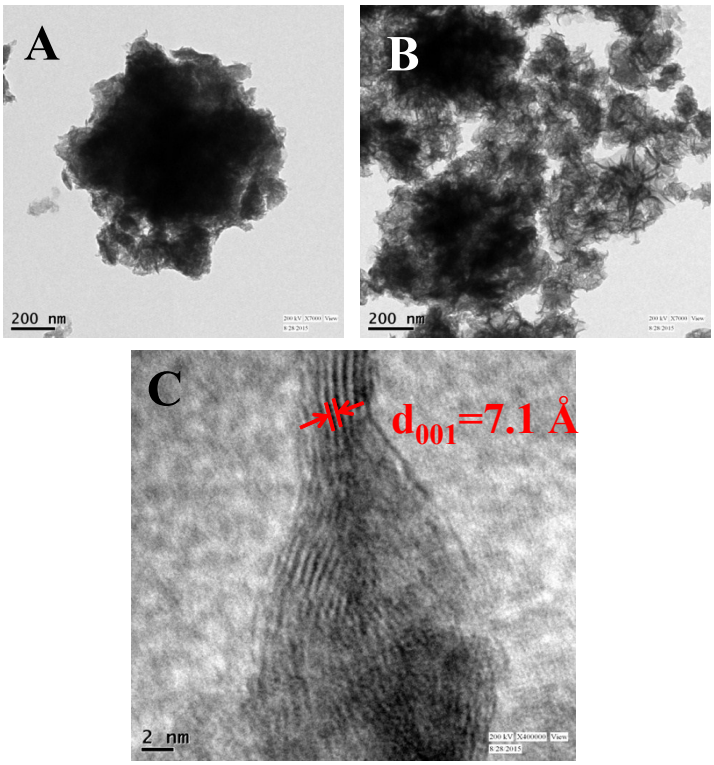


Figure S5

HRTEM images of as-synthesized mesoporous hierarchical δ-MnO_2 nanostructure (obtained at 5:1 molar ratio).

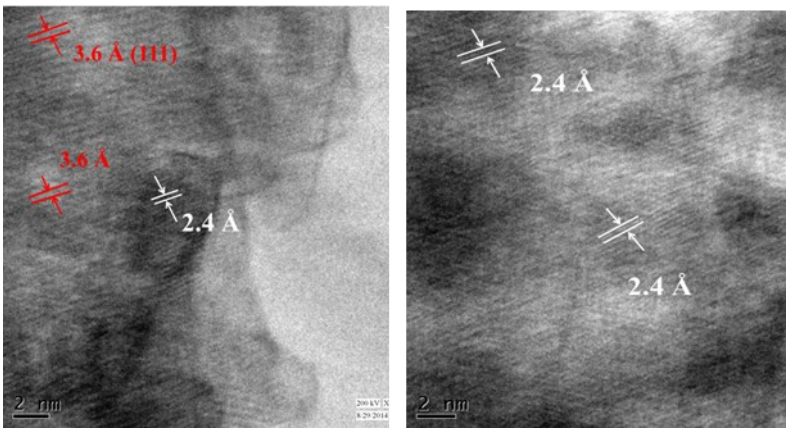


Figure S6

Rate capability of the δ-MnO_2 electrode in 1 M $LiClO_4$ electrolyte.

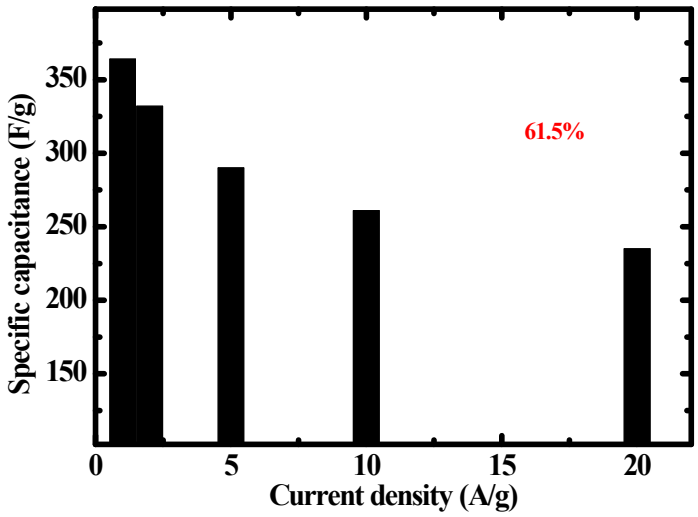


Figure S7

Cyclic voltammogram of mesoporous δ-MnO_2 in 1 M $LiClO_4$, Li_2SO_4, and $LiNO_3$ electrolytes at different scan rate (in three electrode system).

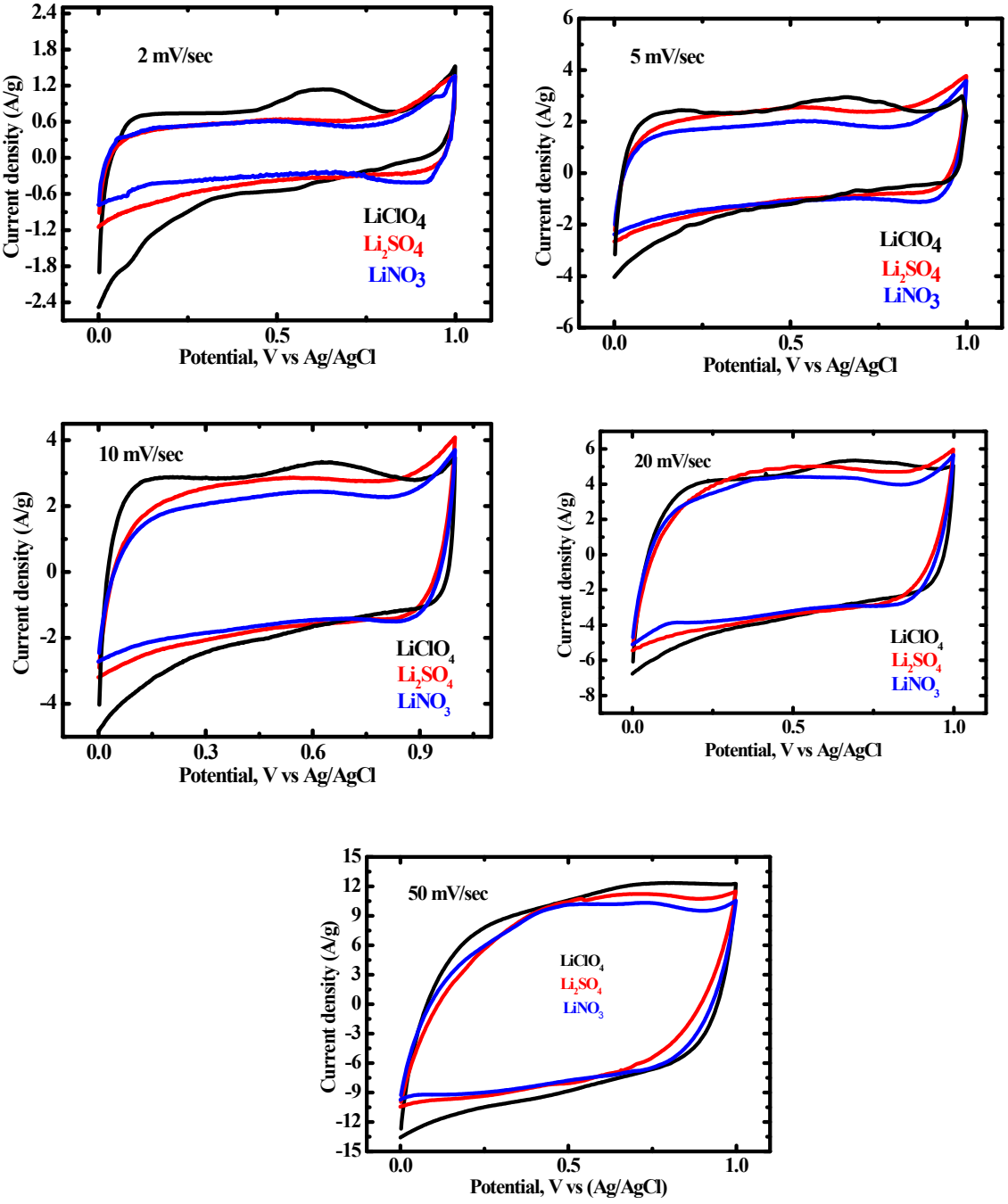


Figure S8

Cyclic voltammetric profile of mesoporous δ-MnO_2 in 1 M $NaClO_4$, Na_2SO_4, and $NaNO_3$ electrolytes at different scan rate (in three electrode system).

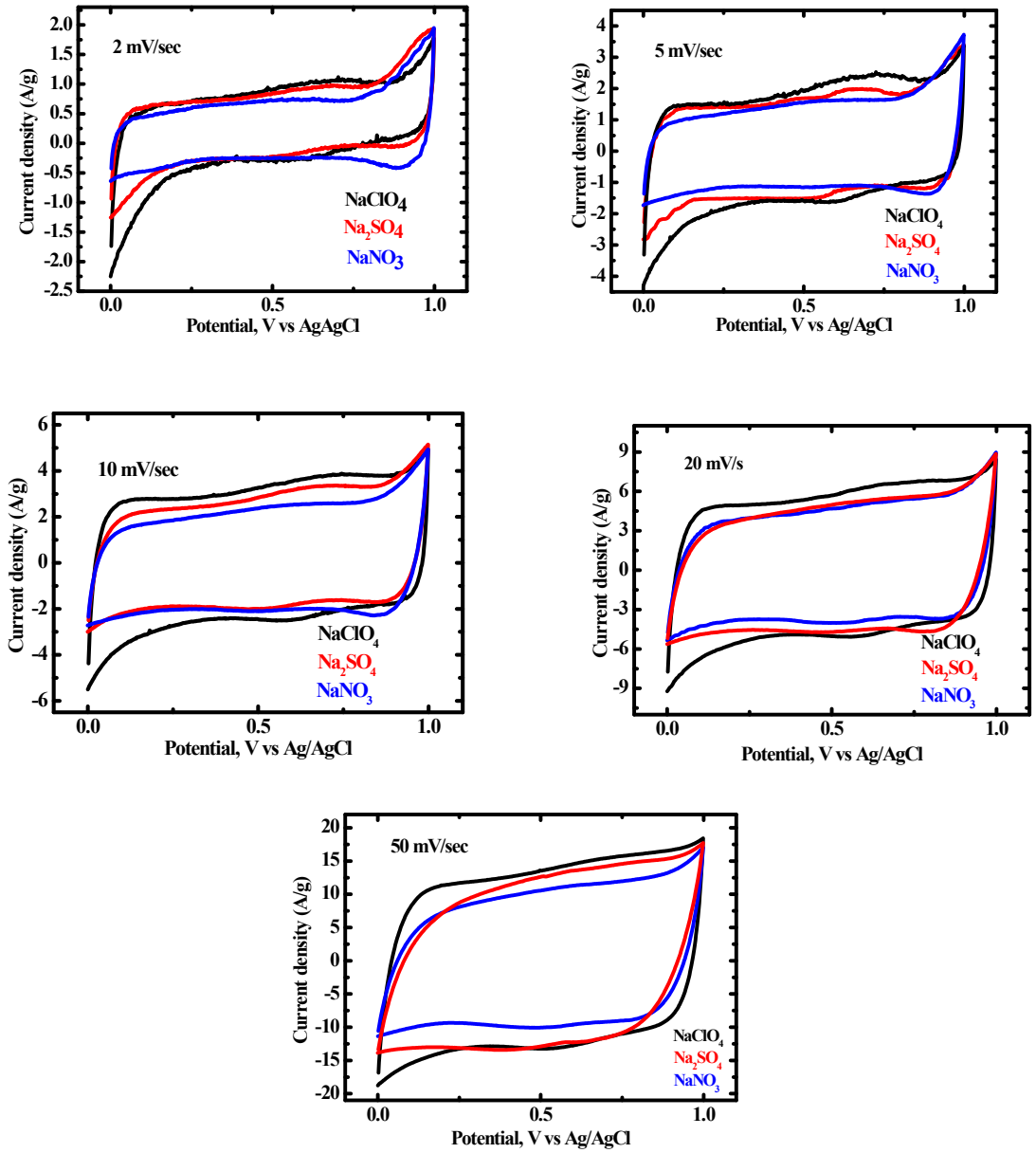


Figure S9

Charge-discharge profile of the mesoporous δ-MnO_2 in different electrolytes.

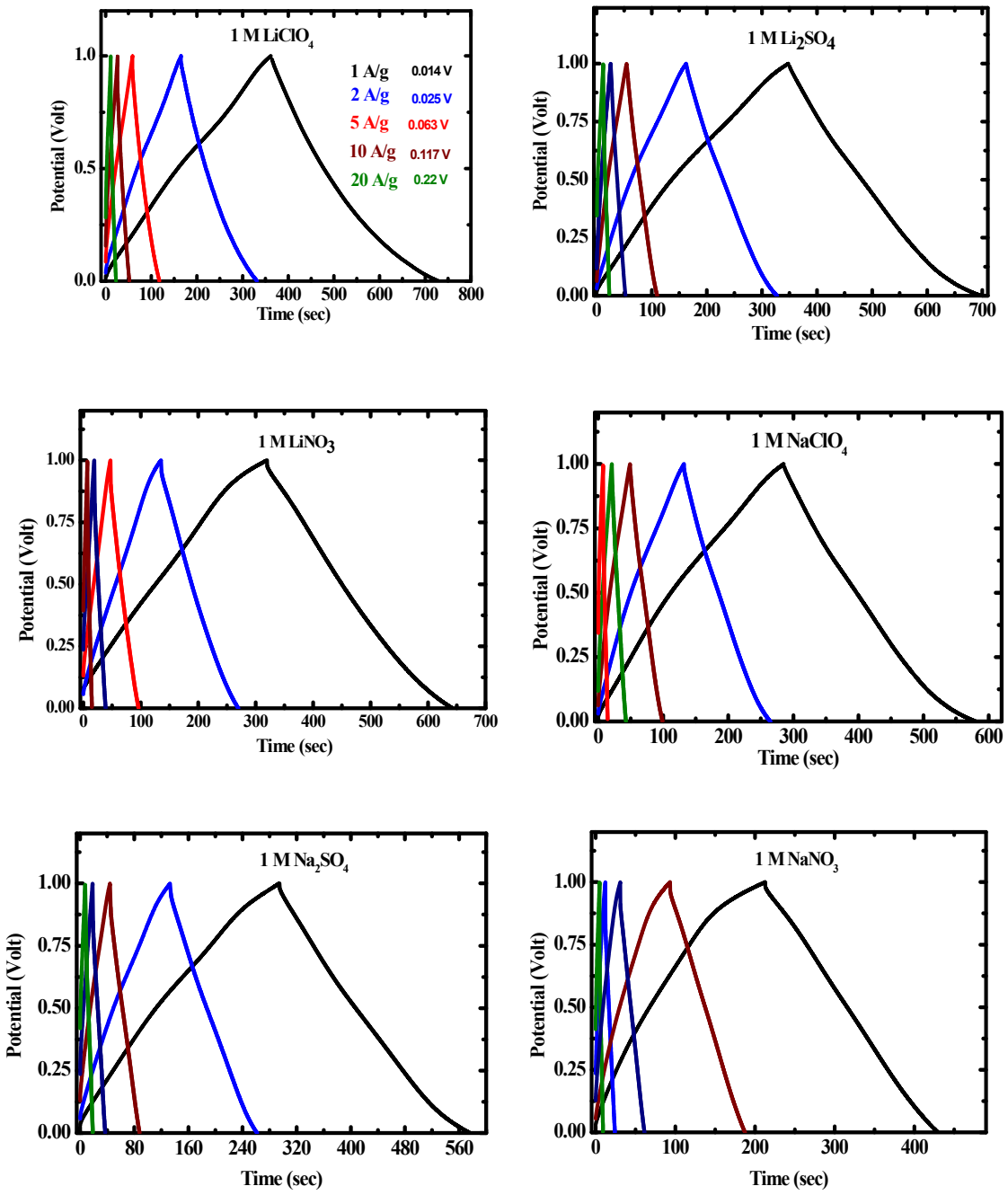


Figure S10

Plot illustrating the cycling stability of various MnO_2 nanostructures: (a) nanoseed, (b) urchin-like (c) 3D hierarchical nanostructures. The specific capacitance was obtained at the current density of 10 A/g in three electrode system. Electrolyte: 1 M aqueous $LiClO_4$.

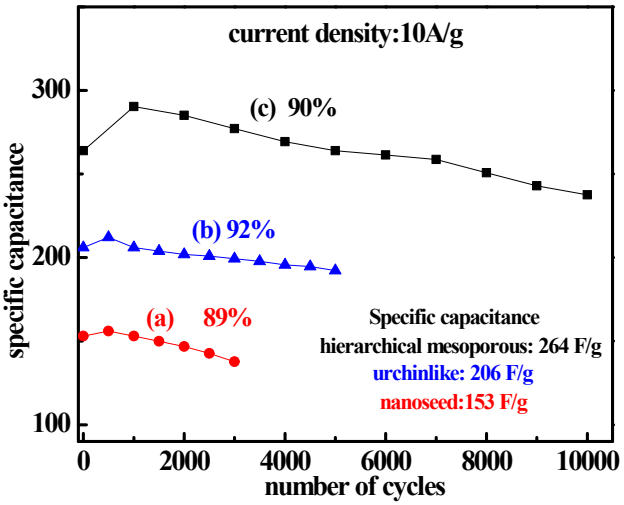
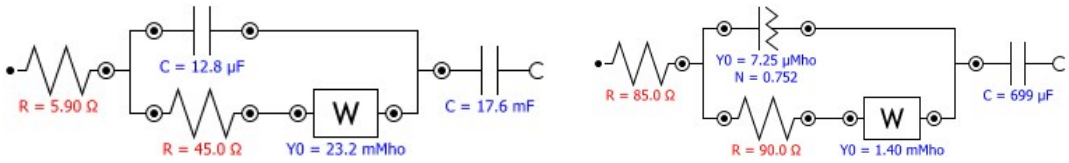


Figure S11

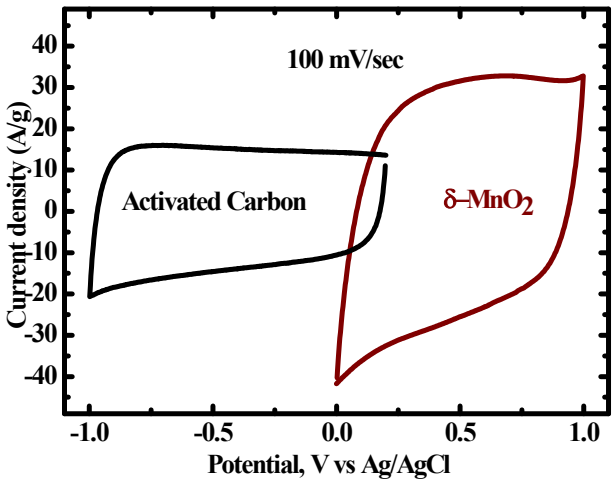
Equivalent circuit used to fit the impedance data before and after 10000 consecutive charge-discharge cycles.



Before charge-discharge **After charge-discharge**

Figure S12

Cyclic voltammogram of activated carbon and mesoporous hierarchical δ-MnO_2 nanostructure in three-electrode system at a scan rate of 100 mV/sec.



The electrodes for the asymmetric supercapacitor device were prepared by following the same procedure as the three-electrode cell experiments. The electroactive material loading on each electrode was controlled by maintaining the charge balance of the two electrodes. The charge accumulated in the cathode (Q_c) should be equal to the anodic charge (Q_a).

To maintain the equal charge balance, $Q_c=Q_a$,

$$m_c Cs_c \Delta V_c = m_a Cs_a \Delta V_a$$

where m_c and m_a are the mass of electrode material in the cathode and anode, respectively. Cs is the specific capacitance of the electrode material. ΔV is the potential window for charge discharge of the corresponding electrode material in three electrode system.

Here, $\Delta V_a = \Delta V_c = 1$ V

$m_c/m_a = Cs_a/Cs_c$

The mass of the active material (m_c) loaded on the Ni foam was ~1 mg. The specific capacitance of the δ-MnO_2 is 362 F/g and the activated carbon is 132 F/g. The amount of

activated carbon taken for the anode is 2.75 mg. The two electrodes were kept in split cell and a filter paper soaked in $LiClO_4$ (1 M) electrolyte was placed between two electrodes.

Figure S13

Nyquist plot and corresponding equivalent circuit obtained with ASC.

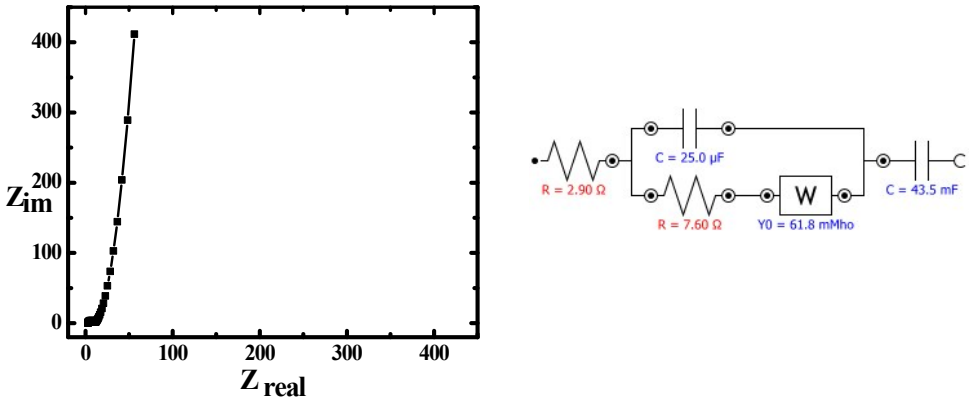


Table S1

Summary of the recent literature on the synthesis of δ-MnO_2

Article	Synthetic strategy	Surface area
Electrochim. Acta 2014,**116,** 188	$KMnO_4$ and thiophene kept in dichloromethane solution and stirred for 24 h at 4°C	226 m^2g^{-1}
Electrochim. Acta 2014,**127** 410	$KMnO_4$ solution having pH ~ 2 was poured into a beaker with the organic solution of dichloromethane and thiophene. The mixed solution was kept at 4℃ for 24 h.	237 m^2g^{-1}
J. Power Sources 2012,**198**, 428	$KMnO_4$ and $MnSO_4{\cdot}H_2O$ (molar ratio is 2:3) are dissolved in water and stirred to form a homogeneous solution, and then the mixture solution is transferred into a Teflon -lined autoclave assembled in microwave oven	213.6 m^2g^{-1}
ACS Appl. Mater. Interfaces 2009,**1**, 1130	$KMnO_4$ and NaOH in water mixed with aqueous solution of $MnCl_2{\cdot}4H_2O$ in 400 mL of water.	45 m^2g^{-1}
J. Mater. Chem., 2010, **20**, 390	30 mg of disordered mesoporous carbon were mixed with 10 mL of aqueous $KMnO_4$ solution of known concentration ranging from 0.001 M to 0.1 M and mixed for 5 min.	186 m^2g^{-1} (with 30% of MnO_2)
Ind. Eng. Chem. Res. 2013, **52**, 9586	NaOH/$MnCl_2$ reflux	49.11 m^2g^{-1}
J. Phys. Chem. C 2008, **112**, 7270	oxidation of the $Mn(OH)_2$ by potassium persulfate $K_2S_2O_8$	20 m^2g^{-1}
Sci. Rep. 2014, **4**, 3878	Reducing $KMnO_4$ in autoclave, polycarbonate template.	85.2 m^2g^{-1}
J. Phys. Chem. B, 2001, **105**, 8712	Fumaric acid is added to a solution of $NaMnO_4$ in a 1:3 molar ratio. Product obtained through gelation takes 24 h	220 $m^2\ g^{-1}$
J. Mater. Chem., 2012, **22**, 153	Graphitic nanorod by CVD + $KMnO_4$ (64% MnO_2)	113 m^2g^{-1}
Mater. Lett. 2010, **64**, 1763	$KMnO_4$ and urea reacted for 24 h at 90°C	230 $m^2\ g^{-1}$
J. Phys. Chem. C, 2007, **111**, 18033	$KMnO_4$ reduction by oleic acid for 10 h at 60 °C	70.70 m^2g^{-1}

This work	Room temperature reduction of $KMnO_4$ by HBr within 2 h	238 m^2g^{-1}

Table S2

Specific capacitance of mesoporous δ-MnO_2 in different electrolytic solution at different current density.

Electrolyte	**Capacitance value (F/g)**				
	1 A/g	**2 A/g**	**5 A/g**	**10 A/g**	**20 A/g**
$LiClO_4$	364	332	290	261	235
Li_2SO_4	348	326	270	248	226
$LiNO_3$	321	266	240	208	170
$NaClO_4$	288	264	242	200	182
Na_2SO_4	282	254	220	190	180
$NaNO_3$	214	186	155	140	120