

Electronic Supplementary Information

**Designed Construction and Validation of Carbon-Free
Porous MnO Spheres with Hybrid Architecture as
Anode for Lithium-Ion Batteries**

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Materials and Methods

Preparation of MnCO₃ microspheres: The solid microspheres of MnCO₃ were synthesized in a mixture of ethanol and water (1:10 v/v) using co-precipitation method. MnSO₄, H₂O, KMnO₄ and Conc. HCl (37% in v/v) were purchased from Alfa Aesar and used without further purification. In a typical procedure, an aqueous solution of NH₄HCO₃ was added to a solution of MnSO₄ in water-ethanol mixture and stirred for 2h to complete the precipitation. The precipitate was then centrifuged, washed and dried to get fine powders of MnCO₃.

MnO porous spheres: For the synthesis of MnO-PS, 1M KMnO₄ (0.035 g) was added to an aqueous dispersion of MnCO₃ (1.82 g). Subsequently, 1M HCl was added drop-wise to the above solution to oxidize the MnO₄⁻ to MnO₂. The solution was subsequently stirred and the resulting brown product was centrifuged and collected. The mass thus obtained was washed thrice with de-ionised water and once with ethanol and dried further at 80 °C in an oven. The dried MnO₂ product was heated in a tubular furnace at 500 °C under argon/hydrogen atmosphere for 6 h to obtain MnO porous spheres. The heating and cooling rates were maintained as 3 °C per minute.

Characterization: X-ray diffraction pattern was recorded with Bruker D8- Advance X-ray diffractometer (Cu-K α radiation; $\lambda = 1.5405 \text{ \AA}$). Unitcell lattice constants were calculated from the XRD data using "unitcell" software. TEM was carried out on a Tecnai instrument operating at 200 KeV. Scanning electron microscopy images were recorded on a Tecnai SEM. FESEM samples were sputter coated with gold and imaged using a Zeiss field emission microscope. X-Ray photoelectron spectroscopy (XPS) data were collected on a Thermo Scientific MULTILAB 2000 Base system with Twin Anode Mg/Al (300/400W) X-Ray Source. Analysis of the collected data was performed using the XPSpeak software. The Raman spectrum was recorded on Renishaw InVia Raman spectrometer with an argon ion laser and charge coupled device detector. Nitrogen adsorption-desorption analysis was carried out using a NOVA 3200e surface area and pore size analyzer. The pore size distribution plot was recorded based on the Barrett–Joyner–Halenda (BJH) model.

Electrochemical Characterization: Electrochemical experiments were performed using CR2032 coin type cells (M/s. Hohsen Corporation). The working electrodes

were prepared by mixing the as-prepared MnO-PS powders, carbon black (Super P) and polyvinylidene fluoride at a weight ratio of 70:20:10 in N-methyl pyrrolidone solvent. Casting the as-obtained slurry over a copper foil using doctor blade method resulted in the formation of uniform coating. The coated material after drying was punched into circular discs with a diameter of 15.45 mm to serve as the anode in lithium ion battery assembly. Polypropylene membrane is used as the separator and the electrolyte consists of a solution of 1M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, in volume, Sigma-Aldrich). Pure lithium foil (Aldrich) was used as counter and reference electrode. The cell assembly was carried out in a glovebox filled with argon (MBraun). The electrochemical properties were examined using Arbin cycler at room temperature between 0.01 V and 3.0 V. Cyclic voltammogram experiment was performed on VSP electrochemical workstation (Biologic) at a scan rate of 0.1 mV s⁻¹ and the electrochemical impedance spectroscopy was carried out on a VMP3 electrochemical workstation (Biologic) in the frequency range of 0.25 MHz to 10 mHz.

Figures

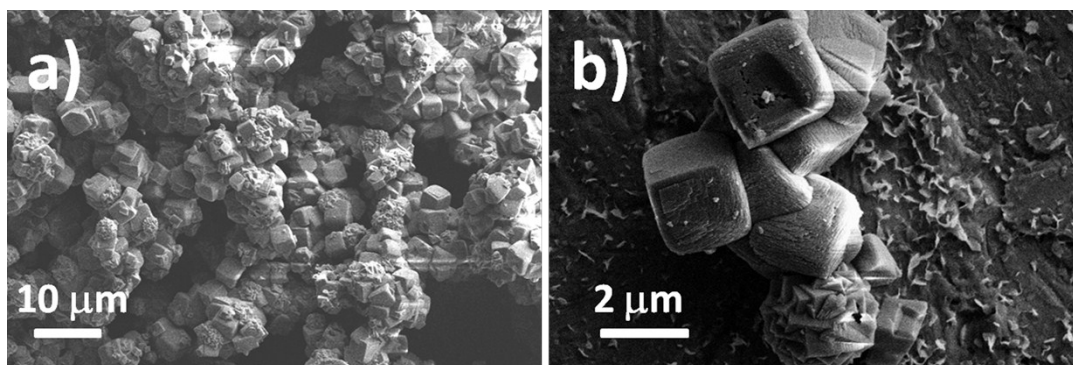


Figure S1. Morphology of MnCO₃ prepared with slow addition of carbonate precursor

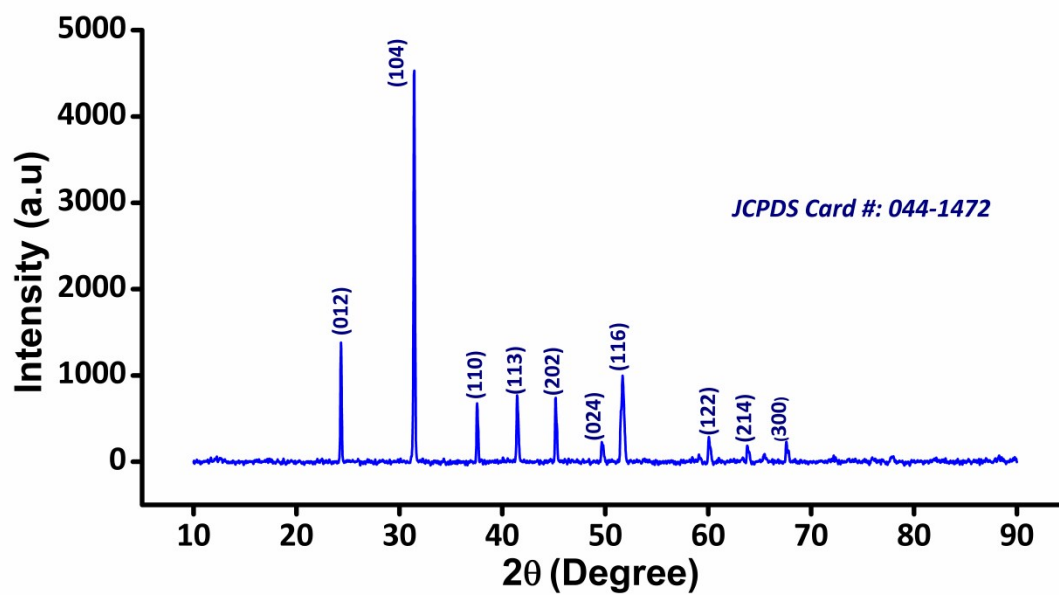


Figure S2. XRD pattern of MnCO₃ precursor.

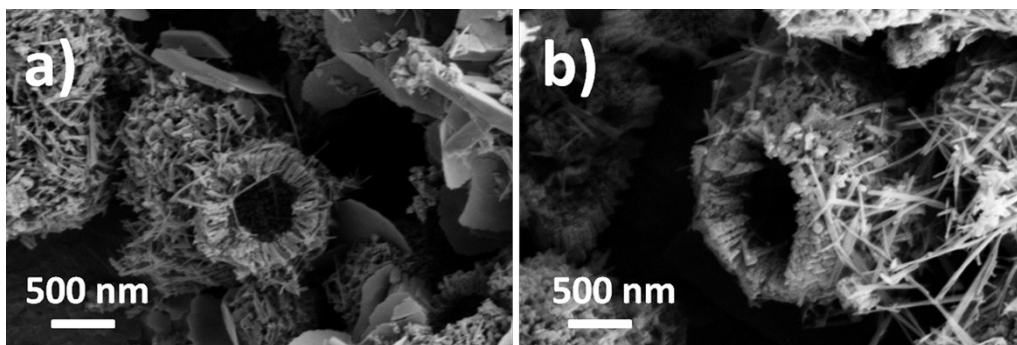


Figure S3. Morphology of MnO_2 prepared with fast addition of KMnO_4

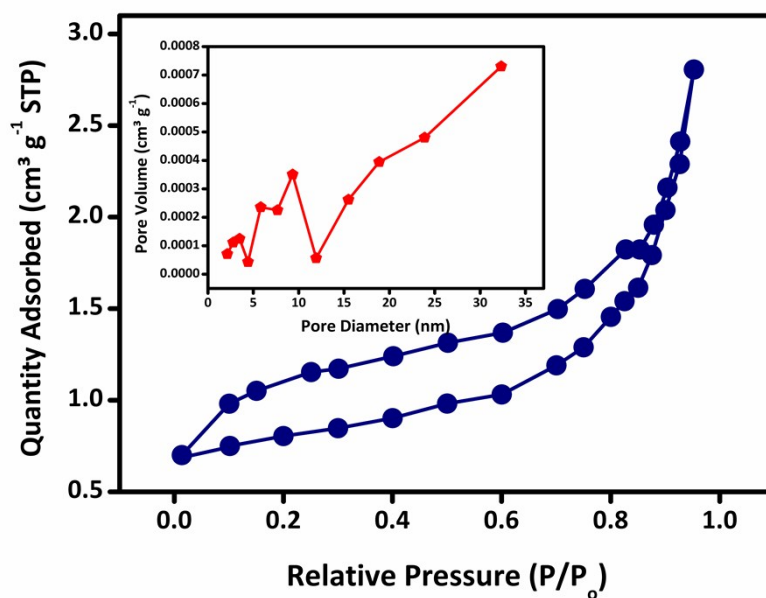


Figure S4. BET Surface area plot of MnO-PS material. Inset displays the pore size distribution curve.

Table 1. Comparison of hkl values obtained from XRD and SAED pattern with reference pattern.

(hkl)	Reference Pattern	XRD	HRTEM (SAED)
(111)	2.568	2.556	2.755
(200)	2.223	2.215	2.199
(220)	1.571	1.568	1.664
(311)	1.340	1.338	1.368
(222)	1.283	1.281	1.234

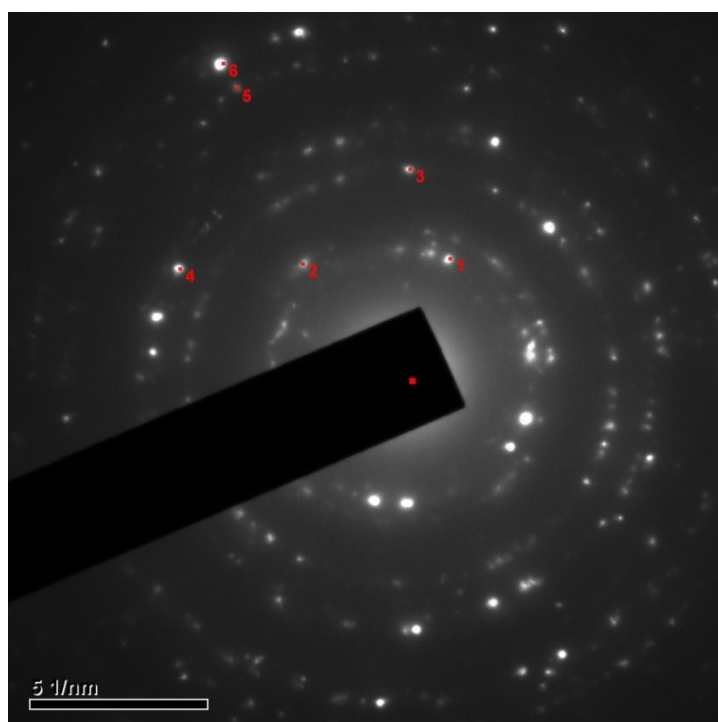


Figure S5. SAED pattern marked with hkl values

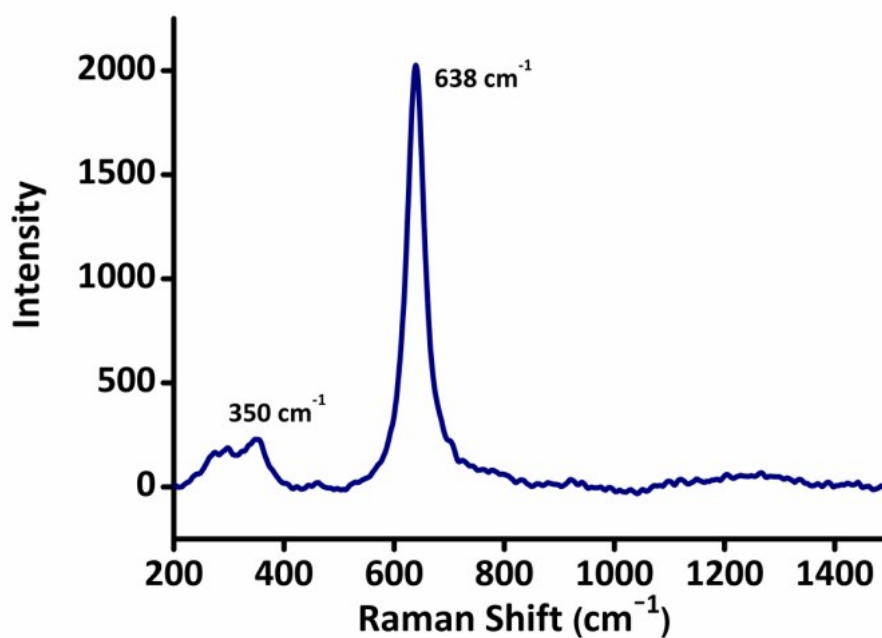


Figure S6. Raman Spectrum of MnO-PS material.

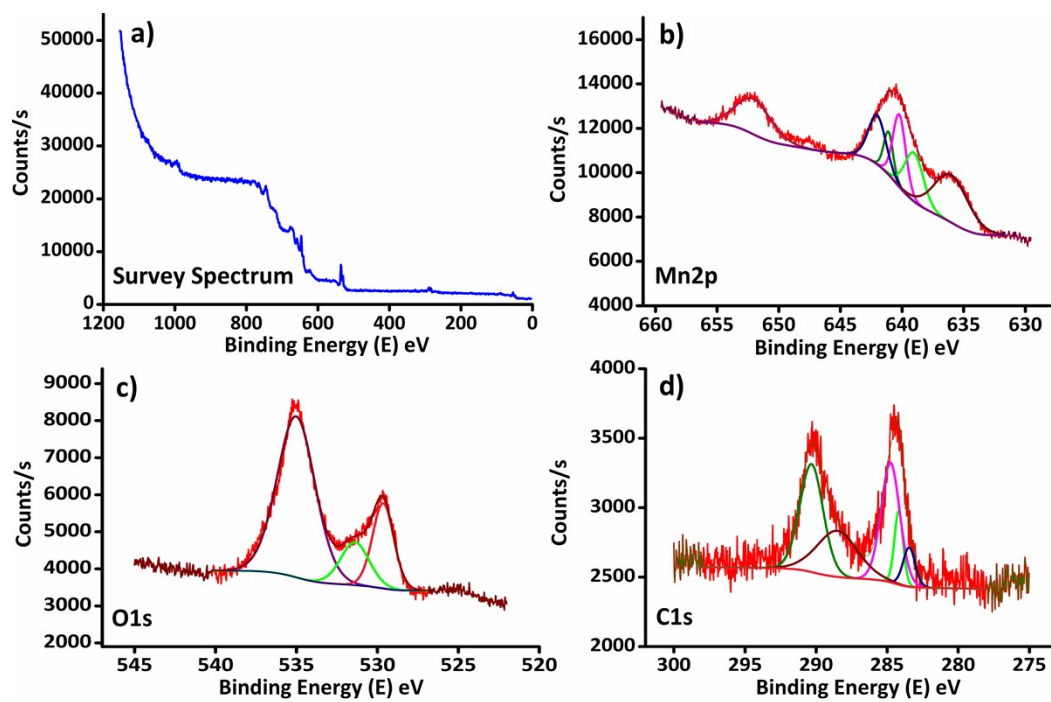


Figure S7. XPS spectra of MnO synthesized by calcination at 500 °C, 4h.

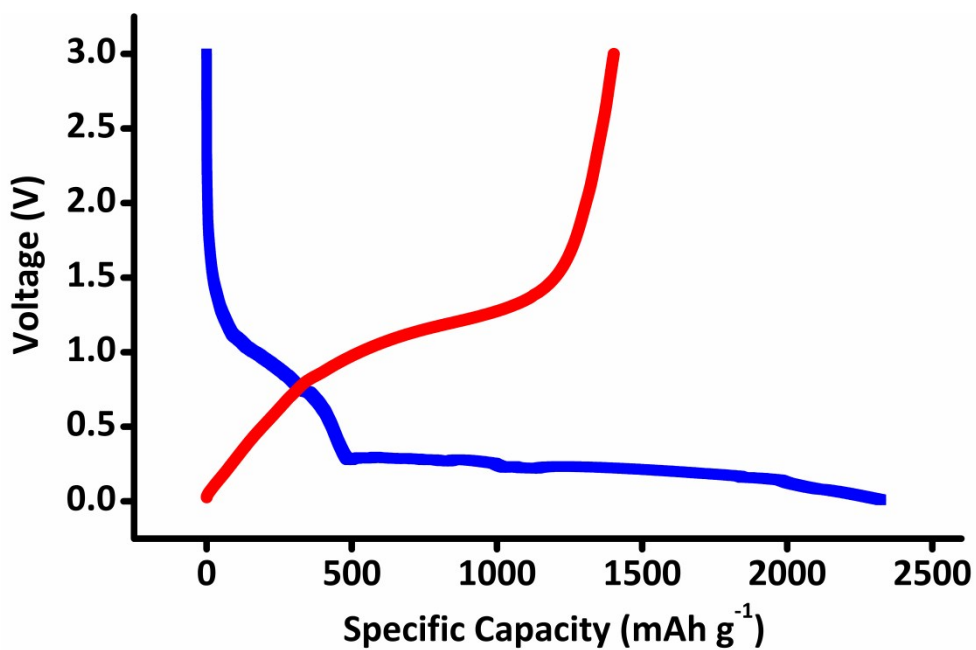


Figure S8. First cycle charge/discharge voltage profile of MnO-PS anode.

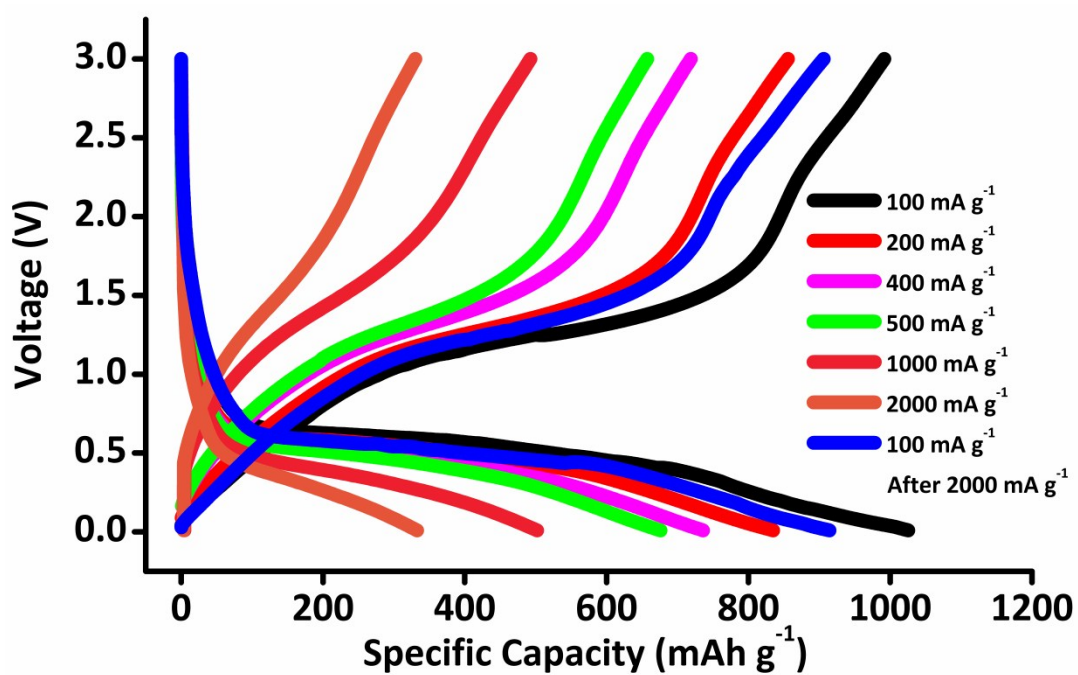


Figure S9. Charge/discharge voltage profile of MnO-PS at different current values.

Table 2. Comparison of discharge capacity values with previous reports

Sl. No	Current Density (mA g^{-1})							Ref. No.
	50	100	200	400	500	800	1000	
1.		1185	912		804		642	[33]
2.		1145	1067		967		822	[34]
3.	682	602	526	432			304	[46]
4.	-	590	479	354	-	238	-	[47]
5.	-	-	-	470	-	320	-	[48]
6.	789	700	570	-	420	-	270	[50]
7.	-	741	611	-	452	-	262	[50]
8.		763	667	604				[51]
9.		650	483	395			299	[52]
10.		750		700			600	[53]
11.	1200	1050	890	785	701		545	This work

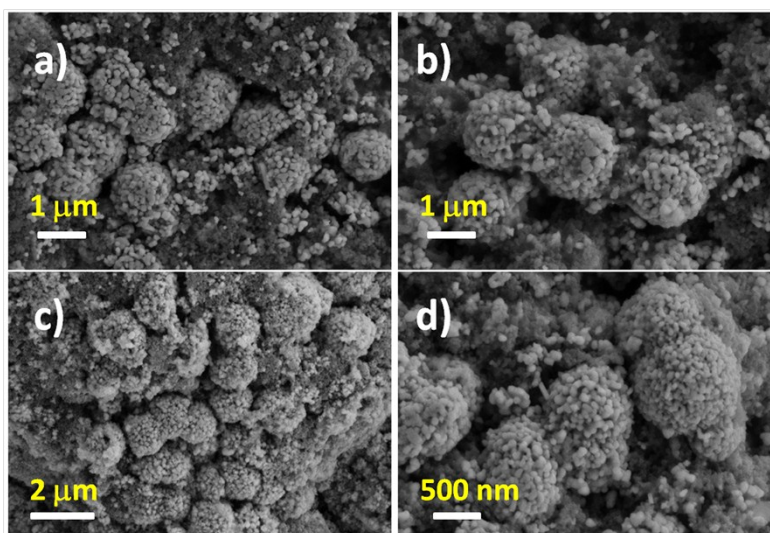


Figure S10. Morphology of MnO-PS anode before cycling (a&b) and after completing 100 charge/discharge cycles (c &d).

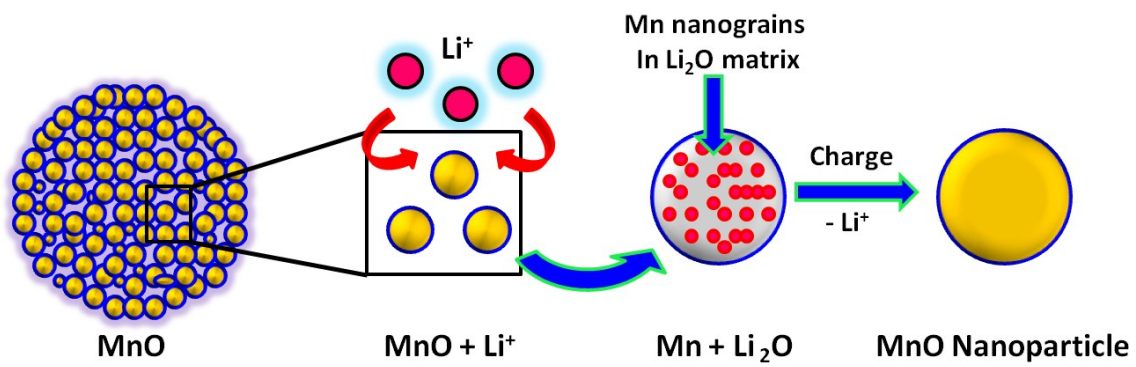


Figure S11. Conversion mechanism associated with the MnO-PS anode of the present study without affecting the morphology upon charge/discharge process, as understood from Fig.S10