Electronic Supplementary Information for

Synthesis of nanostructured P2-$Na_{2/3}MnO_2$ for high performance sodium-ion batteries

Euiyeon Jung,[†ab] Yuwon Park,[†b] Kunsu Park,[†ab] Mi-Sook Kwon,[b] Mihyun Park,[ab] Arun Kumar Sinha,[ab] Byoung-Hoon Lee,[ab] Jiheon Kim,[ab] Hyeon Seok Lee,[ab] Sue In Chae,[ab] Sung-Pyo Cho,[c] Kyu Tae Lee,*[b] and Taeghwan Hyeon*[ab]

[a] Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 08826, Korea.

[b] School of Chemical and Biological Engineering, Seoul National University, Seoul 08826, Korea.

[c] National Center for Inter-University Research Facilities, Seoul National University, Seoul 08826, Korea.

†These authors contributed equally

*Corresponding author: ktlee@snu.ac.kr (K.T.L.), thyeon@snu.ac.kr (T.H.)

Table of Contents

1. Experimental section

Manganese(II) acetylacetonate ($Mn(acac)_2$, 98%), 2,3-dihydroxy naphthalene (2,3-DHN, 90%), benzyl ether (99%), sodium hydroxide (NaOH), and ethylene glycol were purchased from Sigma-Aldrich. Methyl alcohol (MeOH), ethyl alcohol (EtOH), and tetrahydrofuran (THF) were purchased from Samchun Chemicals. All chemicals were used as received without further purification.

1.1. Synthesis of 8 nm MnO_x nanoplates

The synthesis of nanoplates was carried out under an argon atmosphere using the standard Schlenk line technique. In a typical synthesis, 10 mmol of $Mn(acac)_2$ (2.53 g) was added to 50 g of benzyl ether solution containing 30 mmol of 2,3-DHN (4.8 g). The solution was degassed for 2 h at room temperature and then heated to 290 ^oC at the heating rate of 10 ^oC min^{-1}. After reacting at 290 ^oC for 10 min, the solution was naturally cooled to room temperature, and the resulting manganese oxide nanoplates were washed with MeOH and THF several times. The solution was then centrifuged at 1700 rpm for 30 min to produce a brownish solid. The final product was dried in vacuum for the further experiments.

1.2 Synthesis of nanostructured P2-$Na_{2/3}MnO_2$.

1.8 g of MnO_x nanoplates was dispersed in 40 ml THF. Then 30 ml of 1 M NaOH in ethylene glycol solution was added to the dispersed nanoplates. The mixture was then kept at 65 ^oC with vigorous stirring for 48 h. After cooling to room temperature, EtOH was added to the mixture to precipitate the nanoplates, which were then collected after centrifugation at 1700 rpm for 30 min. The resulting product was sintered in air at 500 ^oC for 5 h in a tube furnace to produce the NMO nanoparticles. After sintering, the nanostructured powder was washed with distilled water and another heat treatment was applied at 800 ^oC for 5 h in the same manner to produce the bulk nanostructured P2-$Na_{2/3}MnO_2$ crystals. After each annealing process (500 ^oC and 800 ^oC), the furnace was allowed to cool down to room temperature by natural cooling.

1.3 Material characterization.

The MnO_x nanoplates, NMO nanoparticles and annealed P2-$Na_{2/3}MnO_2$ crystals were characterized by TEM, field emission scanning electron microscopy (FE-SEM), and XRD. The TEM and FE-SEM images were obtained on JEOL JEM-2010 and JSM-6701F microscopes, respectively. Powder XRD patterns were obtained on a Rigaku D/Max-3C diffractometer equipped with a rotating anode and a Cu Kα radiation source (λ = 0.15418 nm). The thin specimens for STEM were prepared by FIB in a FEI Helios Nanolab 650 system. The STEM observations were carried out with a JEOL JEM-ARM200F microscope equipped with a spherical-aberration corrector and a Gatan Image Filter (GIF) for the EELS analysis.

1.4 Electrochemical characterization.

To investigate the electrochemical properties of the P2-$Na_{2/3}MnO_2$ crystals, galvanostatic cycling was performed with a WonATech WBCS 3000 battery measurement system at 30 ^oC. P2-$Na_{2/3}MnO_2$ crystals (70 wt.%), carbon black (Super P, 20 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%) were mixed with N-methyl-2-pyrrolidone as a solvent, and casted on aluminum foil to fabricate the composite electrode. The electrochemical performance of the electrode was examined in a 2032-coin cell with a Na metal anode and 1 M $NaClO_4$ in ethylene carbonate and propylene carbonate (1:1 v/v) electrolyte solution.

2. Figures

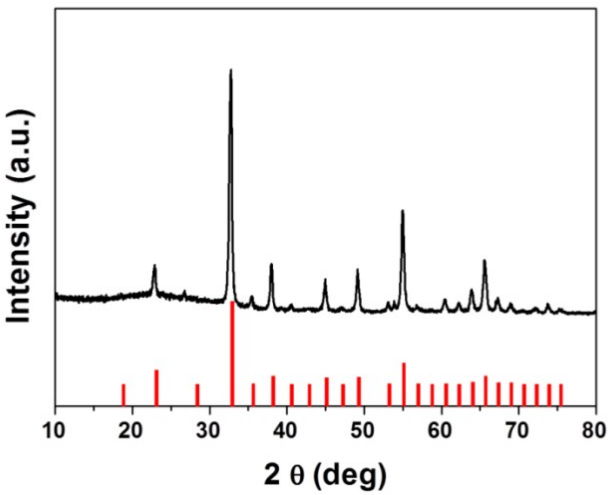

Figure S1. XRD pattern of manganese oxide nanoplates sintered at 500 ºC without the NaOH treatment. The red lines (bottom) are standard XRD pattern of Mn_2O_3 (JCPDS # 24-0508).

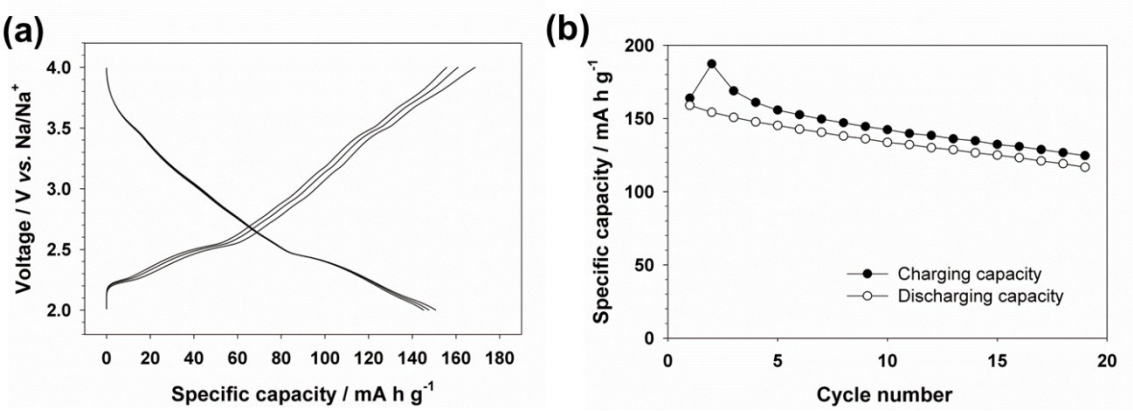

Figure S2. (a) Charge-discharge profiles and (b) cycling performance of sodium manganese oxide nanoparticles at the rate of 12 mA g^{-1}.

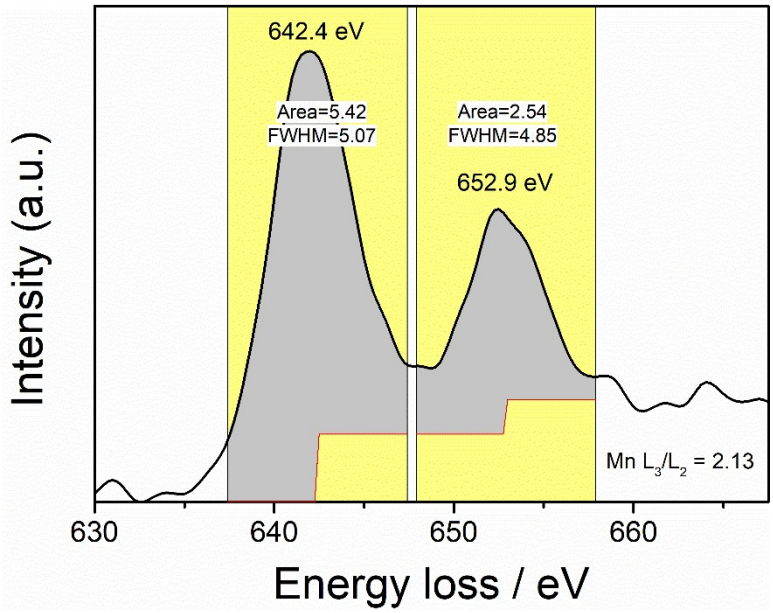

Figure S3. EELS spectrum (first point in Fig. 3f) of Mn-$L_{2,3}$ edges acquired from the as-synthesized nanostructured P2-$Na_{2/3}MnO_2$. Integration window was set as 10 eV centered at peak maxima. Background was set as a double-step function as reported previously (*Appl. Phys. Lett.*, 1988, **53**, 1405; *Phys. Rev. B*, 1993, **47**, 8471). The ratio of the step heights at Mn-L_3 and Mn-L_2 was set as 2:1 according to the

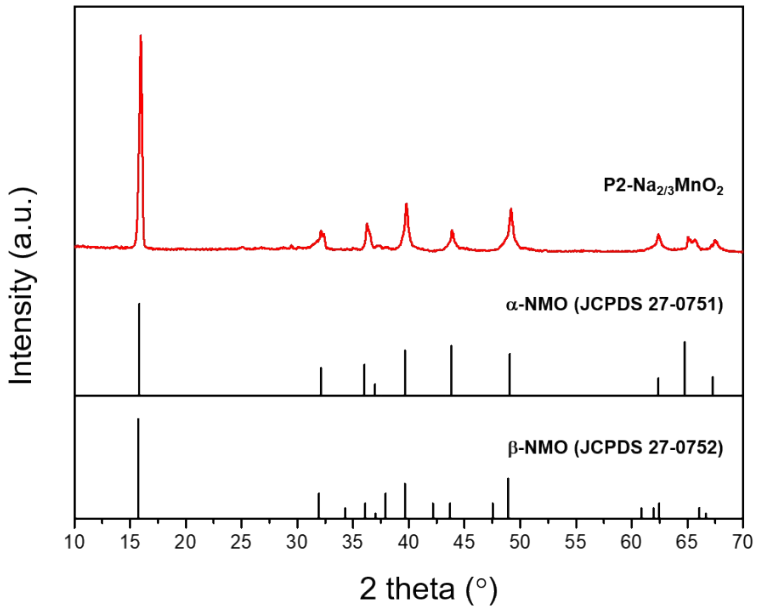

Figure S4. XRD pattern of nanostructured P2-$Na_{2/3}MnO_2$, α-NMO, and β-NMO.

multiplicity of the initial states (four $2p_{3/2}$ electrons and two $2p_{1/2}$ electrons).

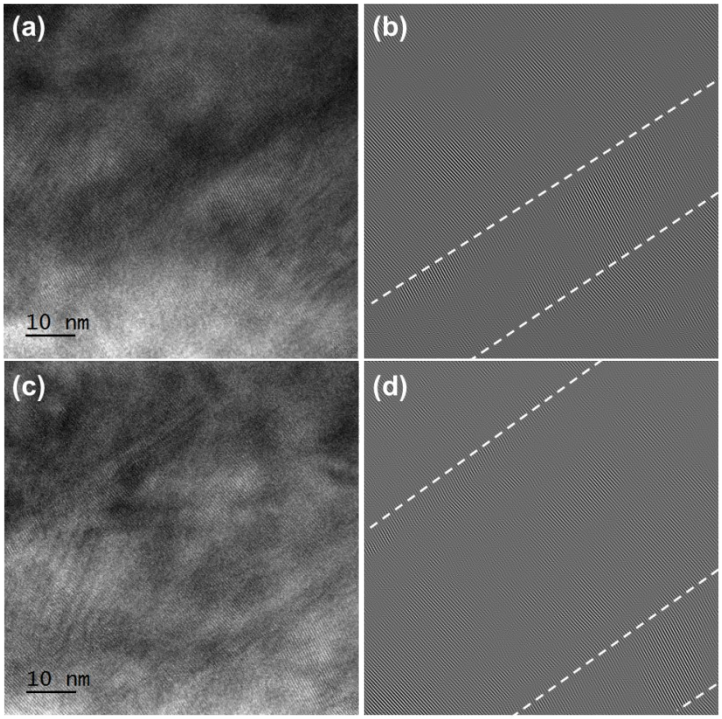

Figure S5. (a), (c) HRTEM images of the bulk nanostructured P2-$Na_{2/3}MnO_2$ crystals, and (b), (d) their inverse fast Fourier transform images.

3. Tables

Position	Mn L_3/L_2 ratio	Mn oxidation state
0.35 nm	2.13	3.67
3.15 nm	2.16	3.59
6.65 nm	2.10	3.74
10.15 nm	2.24	3.39
12.60 nm	2.28	3.29

Table S1. Summary of Mn L_3/L_2 white line ratios and Mn oxidation states derived from an EELS line scan on the nanostructured P2-$Na_{2/3}MnO_2$. Calculated Mn L_3/L_2 ratios were used to derive the corresponding Mn oxidation states using the Mn L_3/L_2 vs. Mn oxidation state curve adapted from a previous report (*Micron*, 2006, **37**,426).

Phase	Initial capacity (mA h g^{-1} / mA g^{-1})	Discharge capacity (mA h g^{-1}) at 50th cycle / capacity retention (%)	Voltage range (V)	Reference
$Na_{2/3}MnO_2$	163 / 18	98 / 60	2.0-4.3	*J. Mater. Chem. A*, 2018, **6**, 8558
	165 / 50	97 / 59	1.5-3.8	*Chem. Mater.*, 2016, **28**, 2041
	140 / 50	75 / 54		
	175 / 12	138 / 79 (25th cycle)	1.5-4.0	*Energy Environ. Sci.*, 2014, **7**, 1387
	170 / 12	140 / 82 (25th cycle)	2.0-3.8	
	140 / 50	87 / 62	1.5-3.8	*ACS Appl. Mater. Interfaces*, 2014, **6**, 8059
	160 / 50	118 / 74		
	140/ 50	75 / 54		
	165 / 40	110 / 67	2.0-4.5	*Chem. Eur. J.*, 2013, **19**, 10884
	170 / 12	**165 / 97**	**2.0-3.8**	**This work**

Table S2. Summary of literature on $Na_{2/3}MnO_2$.