

Supporting Information for “ α -MnO₂ nanowire catalysts with ultra-high capacity and extremely low overpotential in lithium-air Batteries through tailored surface arrangement”

*Kyeongse Song,^{‡,a} Jaepyeong Jung,^{‡,a} Yoon-Uk Heo,^b Yoon Cheol Lee,^a Kyeongjae Cho^{*c,d}
and Yong-Mook Kang^{*a}*

^a Department of Energy and Materials Engineering, Dongguk University-Seoul, Seoul 100-715, Republic of Korea, ^b Research Facility Center, Graduate Institute of Ferrous Technology, Pohang University of Science and Technology Pohang 790-784, Republic of Korea, ^c WCU Multiscale Mechanical Design, School of Mechanical and Aerospace Engineering, Seoul National University, Seoul 151-742, Republic of Korea, ^d Department of Materials Science and Engineering and Department of Physics, University of Texas, Dallas, Richardson, TX 75080, USA

[‡] *These authors contributed equally*, * Corresponding author E-mail: Kyeongjae Cho; kjcho@utdallas.edu, Yong-Mook Kang; dake1234@dongguk.edu

Experiment details

Preparation of α -MnO₂ Nanoparticles: α -MnO₂ nanoparticles were synthesized by a Sol-gel process where an aqueous solution of KMnO₄ (0.2M) was dropwise added to an aqueous solution of Mn(CH₃CO₂)₂ (0.3M) under stirring. The formed precipitate was stirred continuously for 3h before it was removed by filtration, washed, and dried in a vacuum oven at 60 °C overnight. It was subsequently ground into powder and calcined at 300 °C for 3 h to obtain the α -MnO₂ nanoparticle.¹

Preparation of α -MnO₂ Nanowires: Nanocrystalline α -MnO₂ nanowires were synthesized by hydrothermal process a MnSO₄•H₂O (0.1 mol) was dissolved in water (30 ml) and KMnO₄ (0.1 mol) was added under stirring at room temperature. The solution was transferred to a Teflon-lined stainless-steel autoclave with a capacity of 100 mL, sealed and maintained at 140 °C for 12h. After cooling to room temperature, the resulting mixture was separated by centrifugation, washed by water, and then dried in a vacuum at 60 °C for 12h to obtain the α -MnO₂ nanowire.²

Preparation of α -MnO₂ Nanotubes: Nanocrystalline α -MnO₂ nanotubes were synthesized by hydrothermal process HCl (10 mmol) was dissolved in D. I. water (70 ml) and KMnO₄ (2.5 mol) was added under stirring at room temperature. The solution was transferred to a Teflon-lined stainless-steel autoclave with a capacity of 100 mL, sealed and maintained at 140 °C for 12h. After cooling to room temperature, the resulting mixture was separated by centrifugation, washed by water, and then dried in a vacuum at 60 °C for 12h to obtain the α -MnO₂ nanotube.³

Electrochemical Experiment: The electrodes were fabricated by mixing each active material of α -MnO₂, ketjen black (EC600JD) and PVDF-HFP copolymer with a weight ratio

of 40:45:15 using N-methylpyrrolidone (NMP) as a solvent. The resulting slurries were pasted onto carbon paper (GDL; Gas diffusion layer) and then dried in a vacuum oven at 120 °C for 5 h. The carbon loading of electrodes were 0.3 mg. Swagelok-type cells were assembled in an argon-filled glove box (<1 ppm H₂O) for electrochemical characterization. Lithium metal foil was used as a counter electrode, glassfiber disk as the separator and 1M LiCF₃SO₃ in tetraethyleneglycol dimethylether (TEGDME) as the electrolyte. After assembly and sealing, the (assembled/sealed) cell was removed from argon-filled glove box, and then the cell was purged with O₂ gas for 10 minutes at room temperature. Subsequently, the cell was galvanostatically charged and discharged at a various current density at 200 - 5000 mA_{g(carbon)}⁻¹ over a range of 2.0 - 4.5 V. For the stabilization of cycling, the cell was also tested using a constant current - constant voltage (CC - CV) mode with potentiostatic steps at 4.2 V under limited capacity condition (1000 mA_{g(carbon)}⁻¹).

Structural Characterization: The α-MnO₂ nanomaterials were identified by the X-ray diffraction (XRD; Rigaku D/Max-RB diffractometer, using Cu K_α radiation at 40 kV and 100 mA), the field emission scanning electron microscopy (FE-SEM; TESCAN MIRA LMH2, operated at 15 kV). TEM specimen was prepared on the carbon holey grid. The specimen was observed in transmission electron microscope (JEOL JEM-2100F). In order to measure the conductivity of the α-MnO₂ nanomaterials, a Jandel four-point probe technique was adopted. Finally, the pore volume and surface area of our α-MnO₂ nanomaterials were estimated by Barret–Joiner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) analyses, respectively.

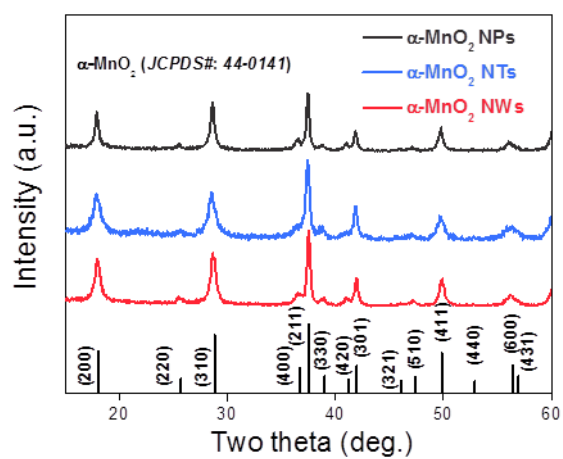


Fig. S1. XRD patterns of α -MnO₂ NPs, α -MnO₂ NTs and α -MnO₂ NWs.

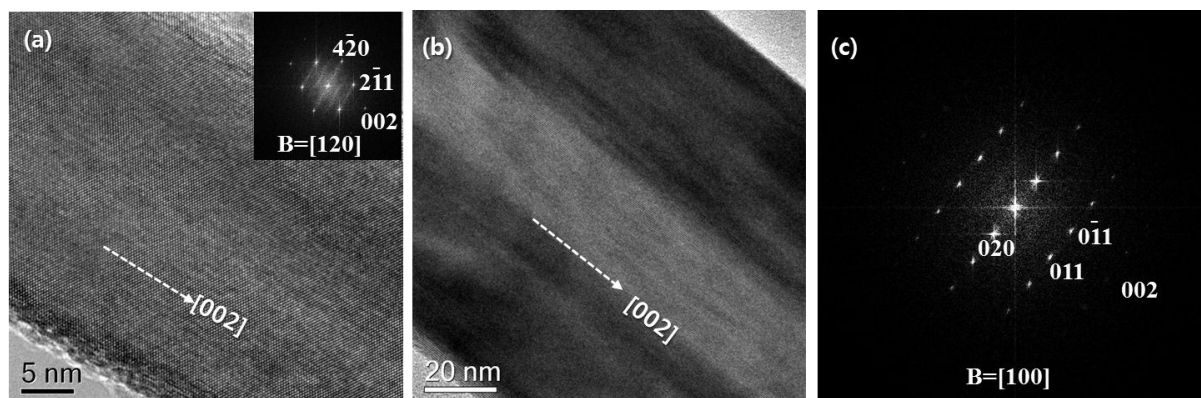


Fig. S2. (a) HRTEM image and FFT in set of a nanowire; growth direction of a nanowire is [002]. (b) HR image and (c) its FFT of a nanotube; growth direction of a nanotube is [002].

Table S1. The atomic concentrations determined by the fitting Mn 2p_{3/2} spectra via Gaussian-Lorentz curve fitting.

	Mn 2p_{3/2} atomic concentration %	
	Mn³⁺	Mn⁴⁺
<i>α</i>-MnO₂ NTs	29.4	70.6
<i>α</i>-MnO₂ NWs	33.4	66.6

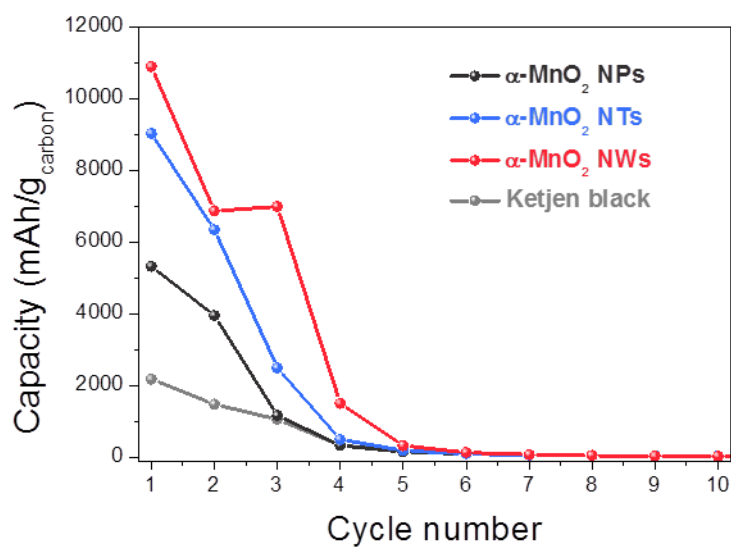


Fig. S3. The electrochemical cyclability of MnO_x nanomaterial at a current rate of 200 mA g_{carbon}⁻¹.

Table S2. Electrical conductivities, Surface areas, and Pore volume of MnO_x nanomaterials.

	Slurry conductivity σ [S·cm ⁻¹]	Surface area [m ² ·g ⁻¹]	Pore volume [cm ³ ·g ⁻¹]
α-MnO₂ NPs	0.8374	174.790	0.461200
α-MnO₂ NTs	0.8487	44.085	0.075460
α-MnO₂ NWs	0.8657	32.512	0.050189

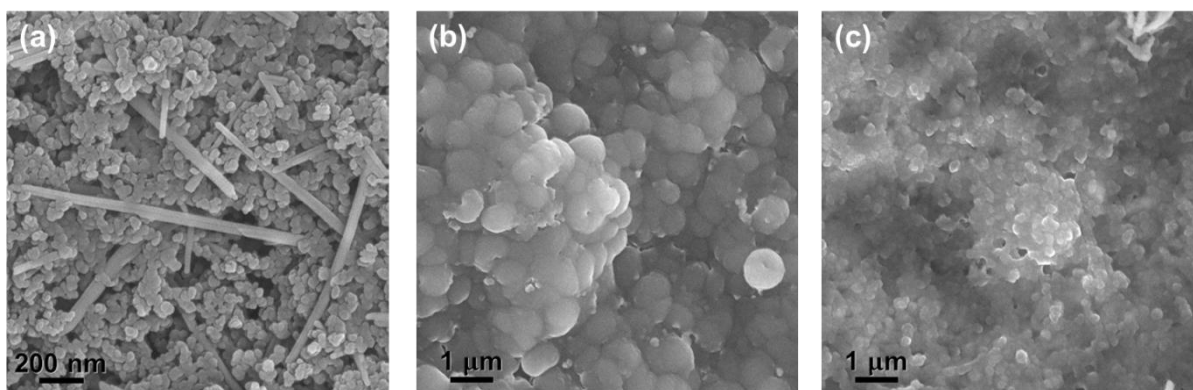


Fig. S4. (a) SEM images of the as-prepared electrode of α -MnO₂ NWs. (b) SEM image of catalyst-free electrode after first discharge. (c) SEM image of α -MnO₂ NPs electrode after first discharge.

References

- 1 H. Y. Lee, J. B. Goodenough, *J. Solid State Chem.* 1999, **144**, 220.
- 2 X. Wang, Y. Li, *Chem. Eur. J.* 2003, **9**, 300.
- 3 J. Luo, H. T. Zhu, H. M. Fan, J. K. Liang, H. L. Shi, G. H. Rao, J. B. Li, Z. M. Du, Z. X. Shen, *J. Phys. Chem. C*, 2008, **112**, 12594.