Electronic Supplementary Information

High aspect ratio γ-MnOOH nanowires for high performance rechargeable nonaqueous Li-O_2 battery

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Experimental Section

Synthesis and characterization of γ-MnOOH nanowires (MNWs)

15.8 mg potassium permanganate ($KMnO_4$) and 7.8 mg polyvinylpyrrolidone (PVP) (Mw=40,000, Aldrich) were dissolved in 15 mL of distill water. After stirring for half an hour, the solution was transferred into a 30 mL Teflon-line stainless steel autoclave and heated at 140 ^oC for 25 h, and then naturally cooled down to room temperature. The precipitates, i.e. MNWs were collected by centrifugation and washed several times with distilled water, followed by freezing dry. Morphologies of the synthesized samples were observed on a field emission scanning electron microscope (FESEM, Hitachi S-4800) and a transmission electron microscope (TEM, Philips TF-F20). The structure of the prepared sample was characterized by powder X-ray diffraction (XRD) using Rigaku-Dmax 2500 diffractometer with a Cu Kα X-ray radiation.

Cyclic voltammetry (CV) test

CV was recorded in a three-electrode cell containing 1 M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in dimethoxyethane (DME) electrolyte. The counter electrode was a platinum foil. The Ag/Ag^+ reference electrode consisted of a Ag wire immersed into 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Sigma-Aldrich) and 0.01 M $AgNO_3$ in DME solution and the potential vs. Li/Li^+ was calibrated against a fresh lithium foil. The working electrode was prepared by drop-casting ultrasonicated inks composed of Ketjenblack EC-600JD carbon black

(KB, Akzo Nobel) or catalyst/KB, Nafion dispersion in absolute ethanol onto a glass carbon disk. CV was tested between 2.0-4.4 V (vs. Li/Li^+) at a voltage sweep rate of 20 mV s^{-1}. During measurements, pure Ar or O_2 was bubbled through the cell at ambient pressure.

Synthesis and characterization of *γ*-MnOOH nanorods (MNRs)

MNRs were synthesized by hydrothermal method. 0.1 mmol $KMnO_4$ and 8 mg PVP were mixed together, then 0.15 mmol $MnSO_4 \cdot H_2O$ was added and the total volume of the dispersion was 15 mL. 10 minutes later, 2 mL ethylene glycol was added by drop. After stirring for 10 minutes, the reaction solution was translated into a 30 mL Teflon-line stainless steel autoclave and heated at 140 °C for 24 h.

Li-O_2 cell measurements

O_2-electrodes were prepared by coating the homogenous ink composed of the mixture of 20 wt% MNWs or MNRs, 70 wt% KB, 10 wt% polyvinylidene Fluoride (PVDF), or 90 wt% KB and 10 wt% PVDF, onto the nickel foam disks. The disks of cathodes were dried at 80 ^oC under vacuum for 12 h to evaporation the N-methyl-2-pyrroli-dinone (NMP, Aladdin Reagent) solvent. The Li-O_2 cell consisted of a lithium metal foil anode, a piece of glass fiber separator and the as-prepared cathode, with 1 M LiTFSI in propylene carbonate (PC) or DME as electrolyte. All cells were assembled and disassembled in an argon-filled glove box with oxygen and water contents below 1 ppm. The galvanostatic discharge/charge tests were conducted on a LAND CT2001A multi-channel battery testing system with the voltage between

2.2-4.4 V (vs. Li/Li^+). To avoid complications related to CO_2 and H_2O contamination, the cells were tested in 1 atm of pure O_2. To observe the morphologies of O_2 electrodes after discharge, the cells were first disassembled in the glove box, and then the O_2 electrodes were ringed three times with DME. After removing the solvent under vacuum, the electrodes were introduced into the SEM.

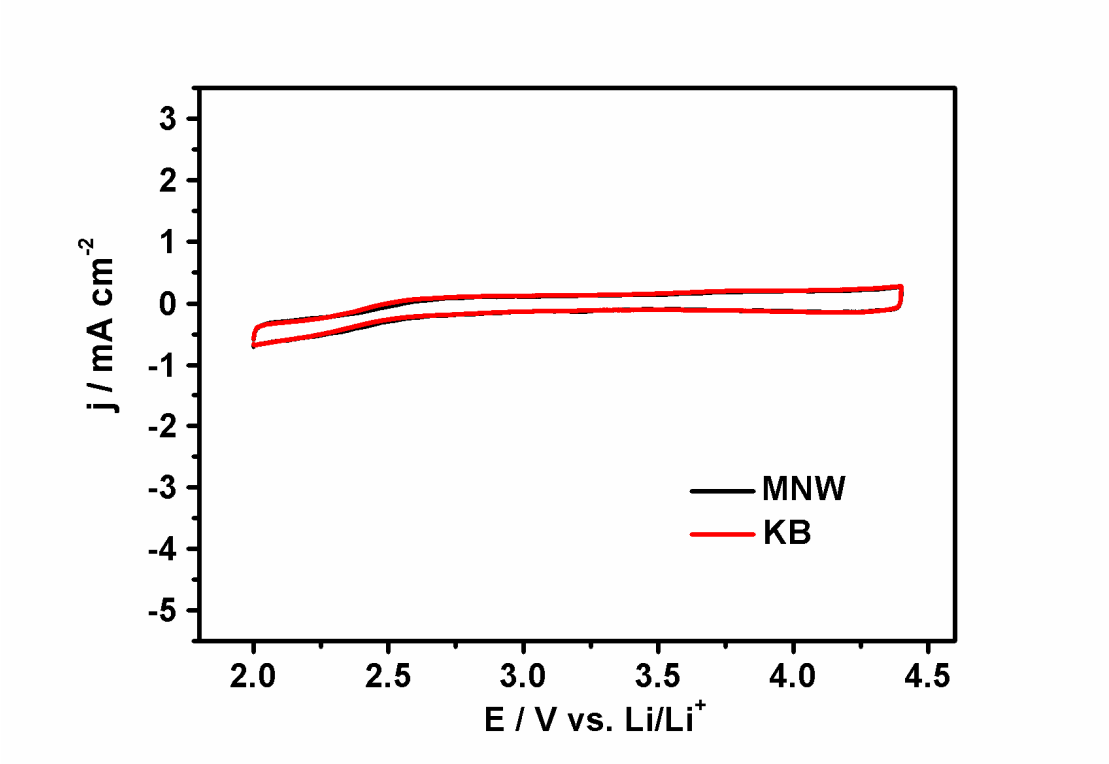

Fig. S1 CV curves of MNWs and pure KB in Ar saturated 1M LiTFSI/DME electrolyte at scan rate of 20 mV s^{-1}.

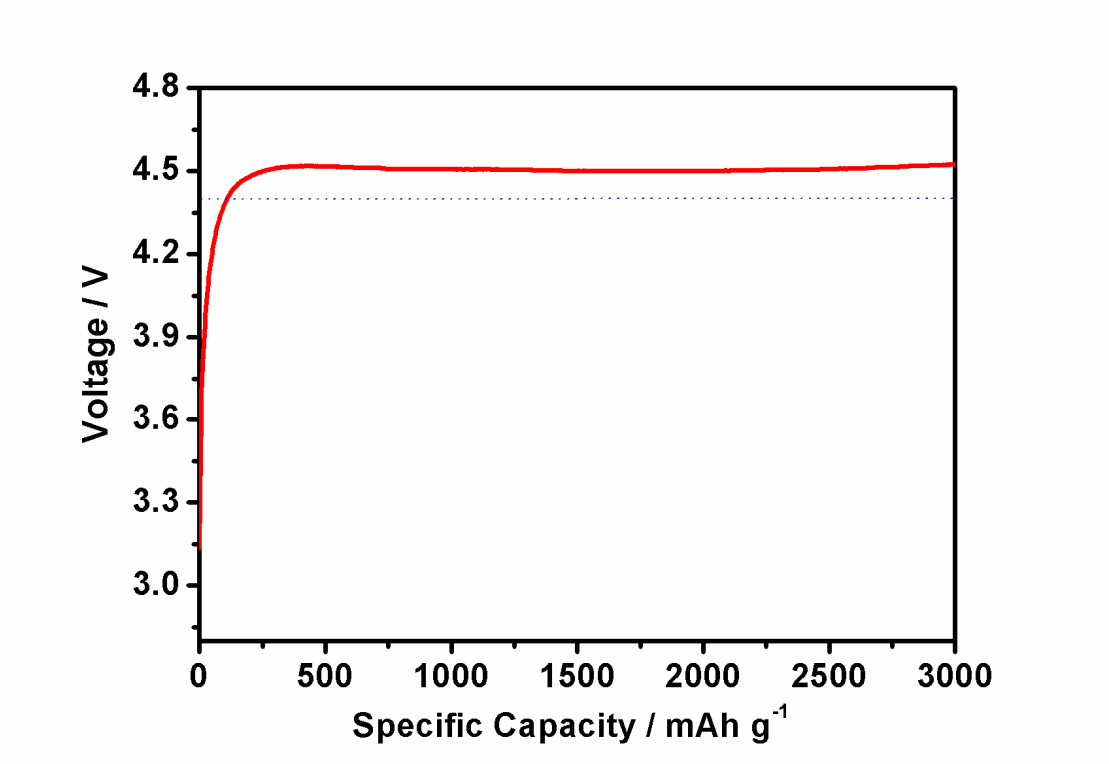

Fig. S2 Background measurement during charging at 0.05 mA cm^{-2} of an O_2-filled cell (charging first) for MNWs in 1 M LITFSI/PC (the voltage of the dotted line is 4.4 V). The result reveals that the charge associated with electrolyte decomposition on MNWs becomes significant at voltage of about 4.5 V.

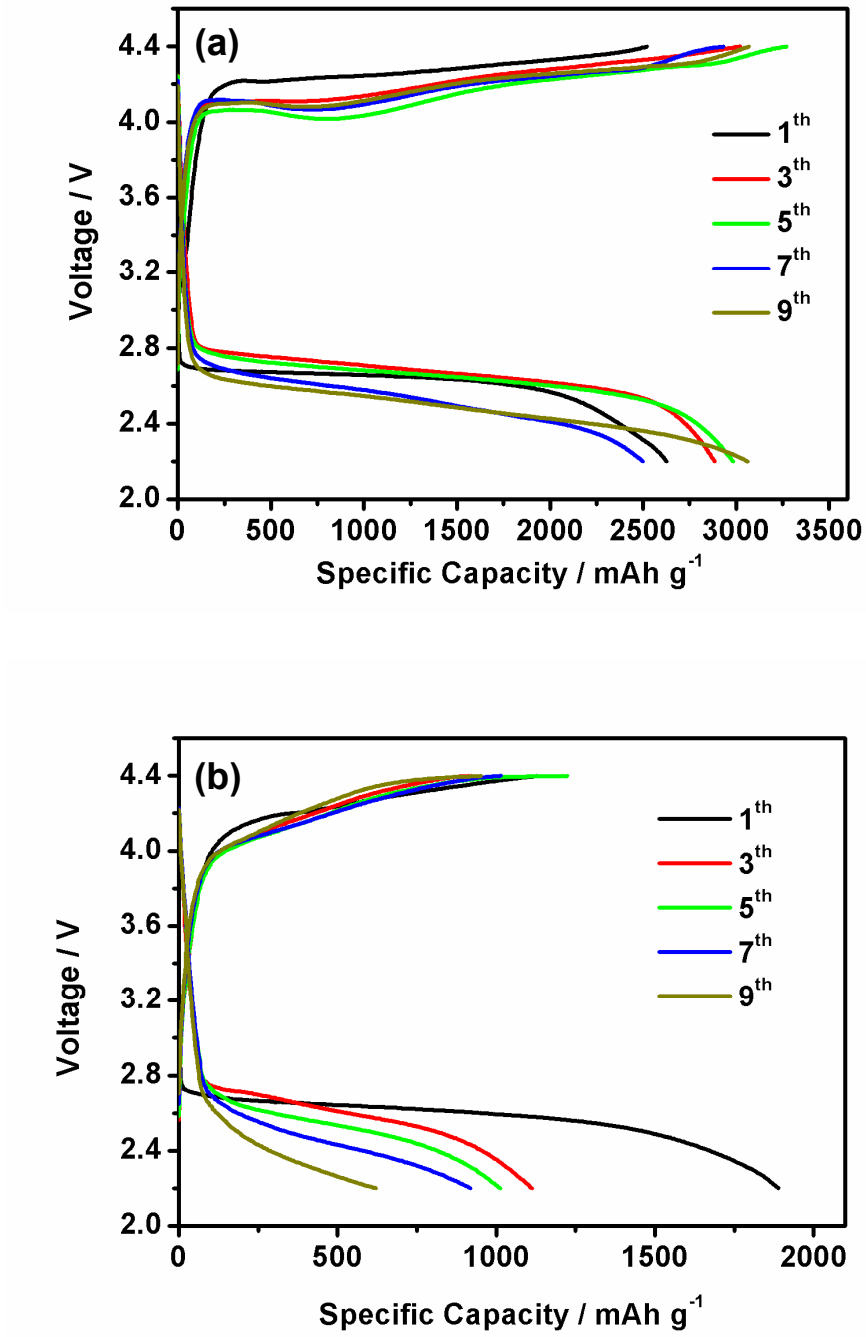

Fig. S3 The discharge/charge curves of (a) MNWs/KB and (b) pure KB electrode at the current density of 0.05 mA cm^{-2}. The capacity and discharge voltage of pure KB decrease seriously with the increase of cycle number.

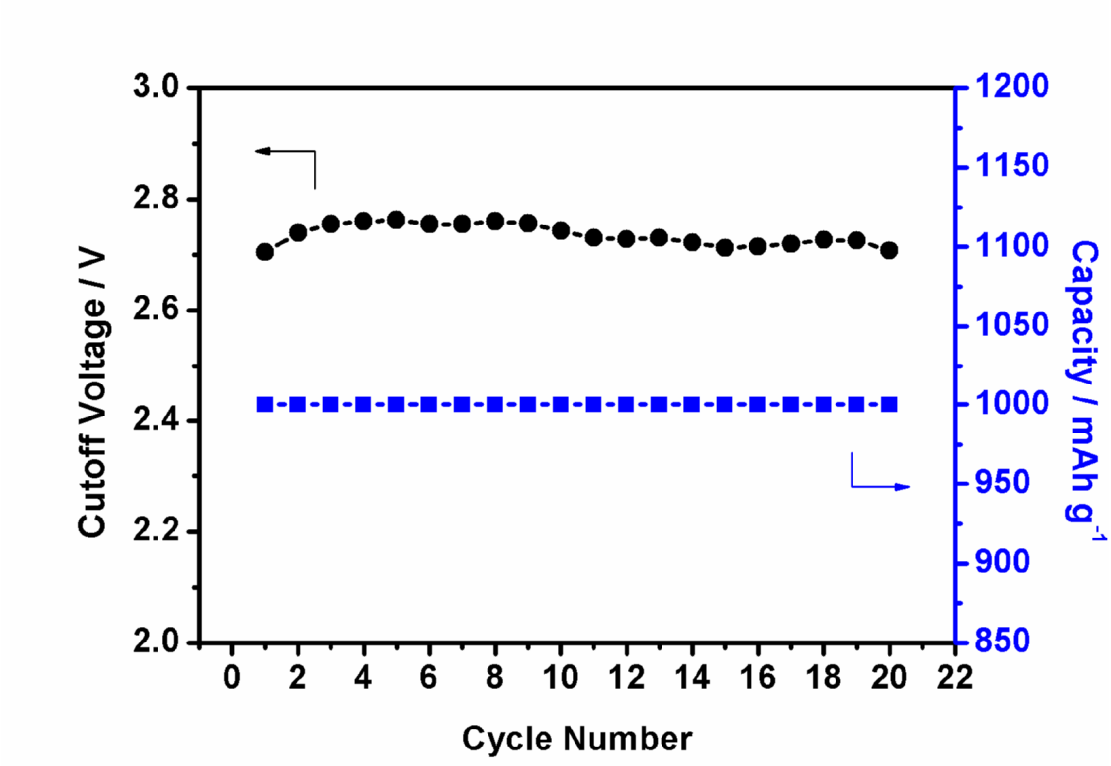

Fig. S4 Cycle performance of MNWs/KB with a restriction of the capacity to 1000 mAh g^{-1} at a current density of 100 mA g^{-1} (squares) and the resulting cutoff voltage of discharge (cycles). By restricting the capacity, the cell exhibits good reversibility, as the cutoff voltage does not change dramatically after 20 cycles. This result is similar to those reported by Cui et al.[1] and Dai et al.[2]

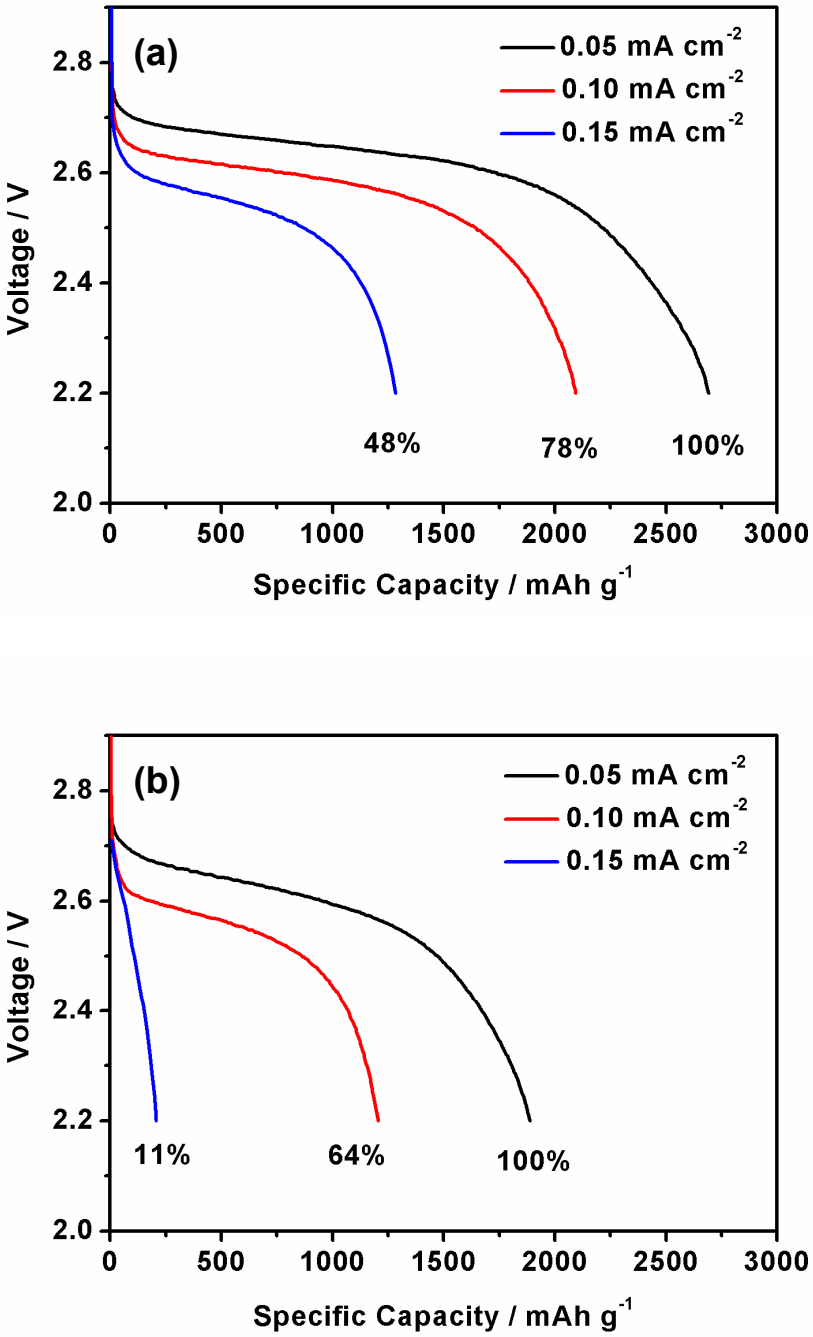

Fig. S5 The discharge curves and capacity retentions of (a) MNWs/KB and (b) pure KB at different current densities. The discharge capacity and discharge voltage decrease quickly of pure KB, especially when the current density is over 0.15 mA cm^{-2}.

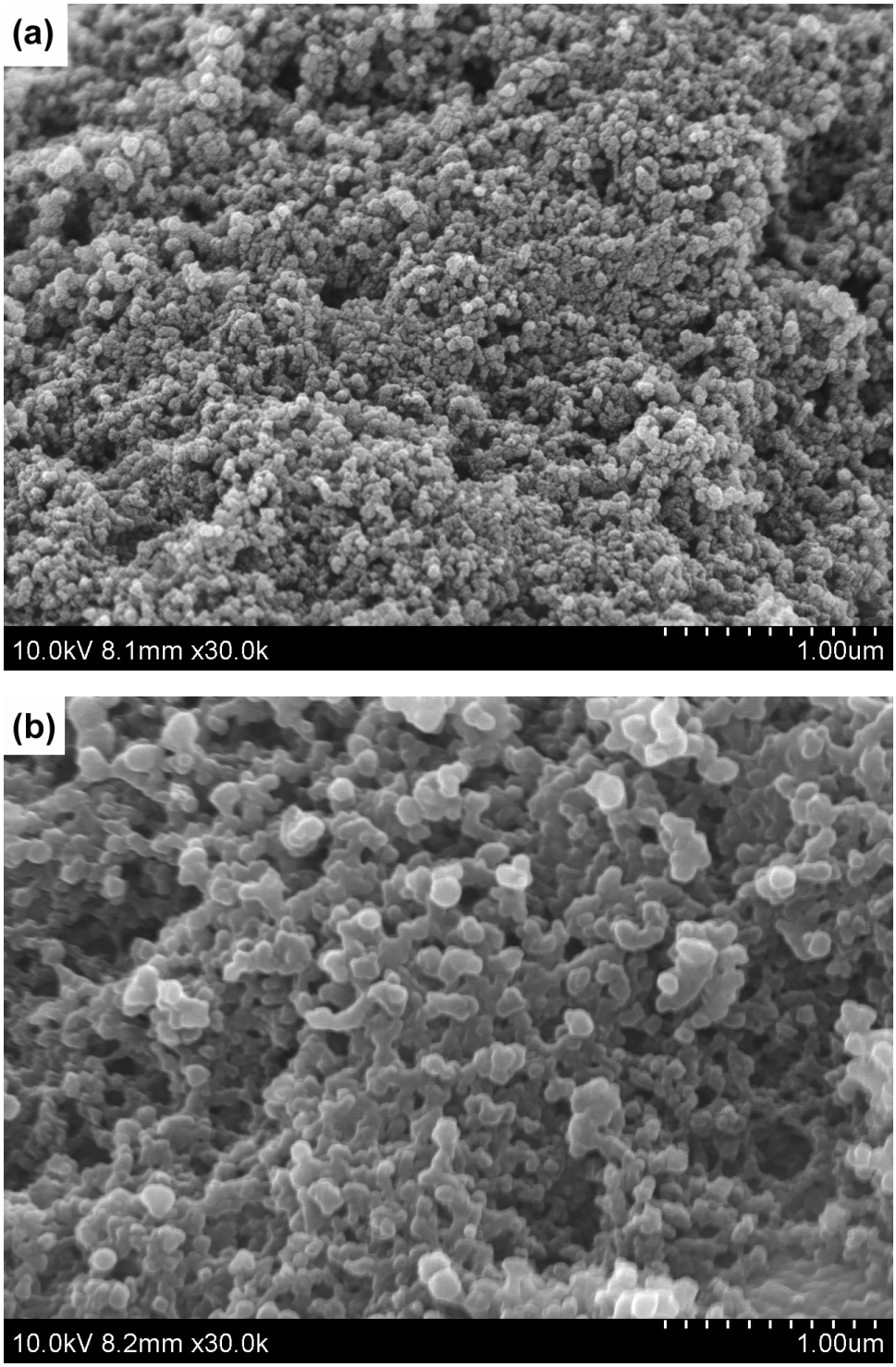

Fig. S6 SEM images of the cathode (a) before and (b) after discharge with pure KB.

Both of them are thick and compact.

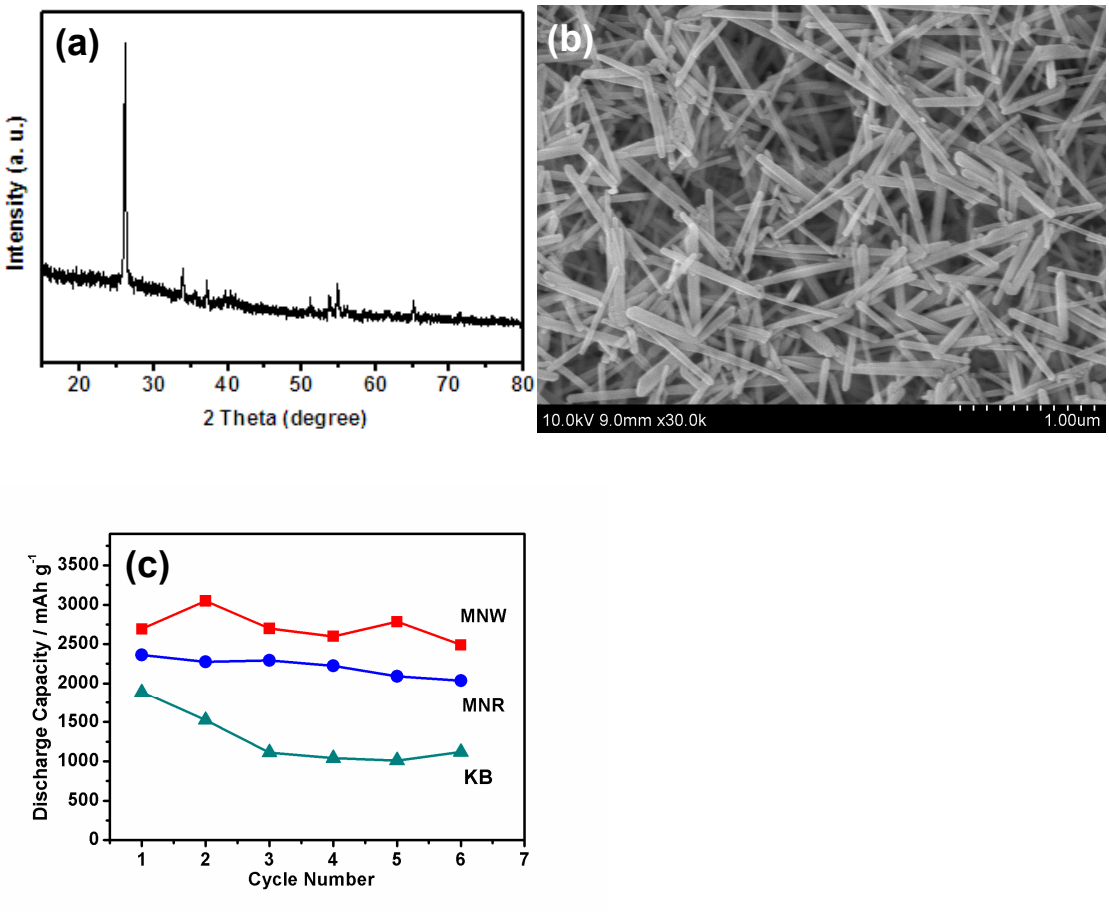

Fig. S7 (a) The XRD pattern and (b) SEM image of MNRs. (C) variation of discharge capacity with cycle number at a current density of 0.05 mA cm^{-2}. All diffraction peaks match well with the monoclinic γ-MnOOH structure (JCPDF No. 41-1379). The MNRs are typically 50 nm in diameter and less of 1 μm long. The corresponding aspect ratio (less than 20) is much lower than that of MNWs. The capacities of MNRs are lower than that of MNWs, but higher than that of pure KB.

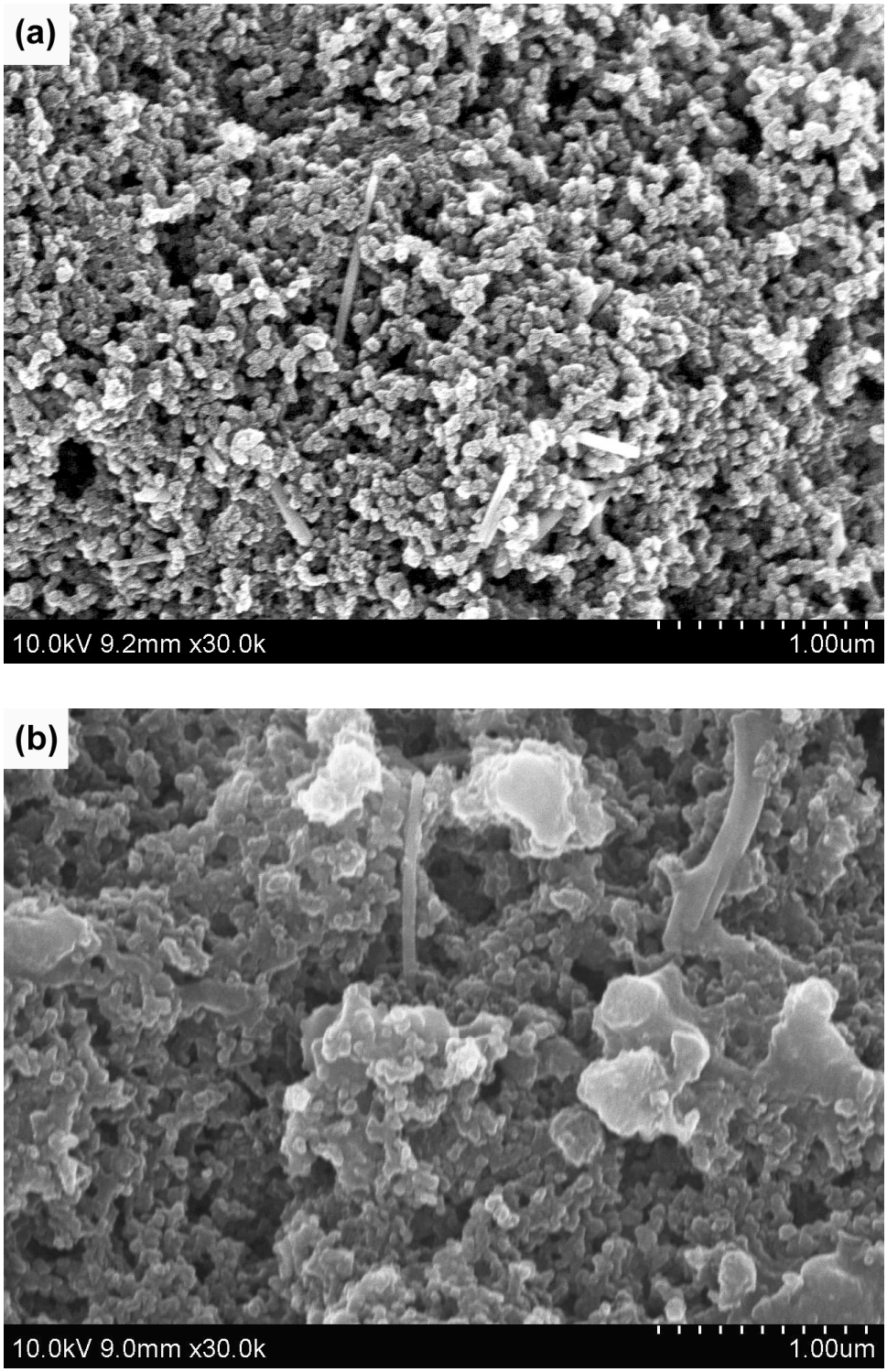

Fig. S8 SEM images of the cathode (a) before and (b) after discharge with MNRs as catalysts. Many nanorods are buried by KB particles, so we can see only a few of them on the surface of electrode. After discharge, the electrode is covered closely with the discharge products.

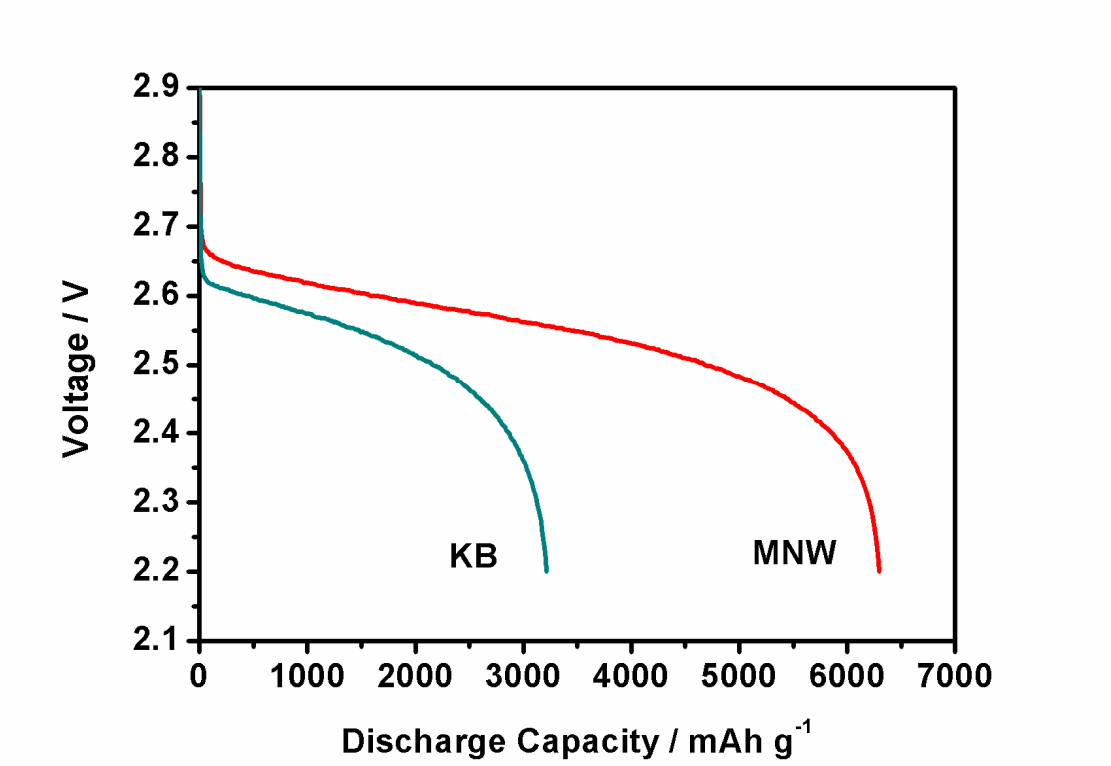

Fig. S9 The first discharge curves of Li-O_2 cells for MNWs/KB and pure KB at the current density of 0.2 mA cm^{-2} in the electrolyte of 1 M LiTFSI/DME. The discharge capacity of the cell with MNWs is 6293 mAh g^{-1}, nearly two times of that with pure KB. And the discharge potential is also obviously higher than that of pure KB.

Table S1 The comparison of capacity retention of Li-O_2 cells for MNWs/KB and pure KB.

O_2 electrode	Discharge capacity (mAh g^{-1})		Capacity retention
	0.2 mA cm^{-2}	0.5 mA cm^{-2}	
MNWs/KB	6293	2874	46 %
KB	3213	581	18 %

When increased the current density from 0.2 mA cm^{-2} to 0.5 mA cm^{-2}, the discharge capacity keeps 46 % of the cell with MNWs as catalyst, while only 18 % with pure KB.

References

1. S. Dong, X. Chen, K. Zhang, L. Gu, L. Zhang, X. Zhou, L. Li, Z. Liu, P. Han, H. Xu, J. Yao, C. Zhang, X. Zhang, C. Shang, G. Cui and L. Chen, *Chem. Commun.*, 2011, **47**, 11291-11293.

2. H. L. Wang, Y. Yang, Y. Y. Liang, G. Y. Zheng, Y. G. Li, Y. Cui and H. J. Dai, *Energy Environ. Sci.*, 2012, DOI: 10.1039/C2EE21746E.