Electronic Supplementary Information for

In-situ imaging electrocatalysis in a K-O_2 battery with hollandite α-MnO_2 nanowires air cathode

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1. Experimental Section

Synthesis of α-MnO_2 NWs

The α-MnO_2 NWs were prepared by a hydrothermal method. The steps are described as follows: commercial $KMnO_4$ (0.5 g, China National Pharmaceutical Industry Co., Ltd.) and $MnSO_4 \cdot H_2O$ (0.34 g, China National Pharmaceutical Industry Co., Ltd.) were dissolved in a 70 mL deionized water with constant electromagnetic stirring for 30 min. Then, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 12 h. After cooling to room temperature naturally, the attained brown material was centrifuged and washed for several times with deionized water and ethanol. The final α-MnO_2 was obtained by drying in an oven at 80 °C for 12 h.

Characterization

The morphology and microstructure of α-MnO_2 nanowires were characterized by Cs-corrected transmission electron microscopy (ETEM, FEI Titan G2, 300 kV). The crystalline structure of α-MnO_2 nanowires were studied by X-ray diffractometer (XRD, Bruker D8 Advance). The elemental content of α-MnO_2 was measured by energy-dispersive X-ray spectroscopy (EDS, equipped in TEM, FEI Tecnai F20, 200 kV). The structure of the sample is identified by using selected area electron diffraction (SAED, equipped in TEM, FEI Tecnai F20, 200 kV) patterns. The composition and valence state of the end product of the discharge reaction were identified by electron energy loss spectroscopy (EELS, equipped in ETEM, FEI Titan G2, 300 kV) characterization and annular dark field (ADF, equipped in ETEM, FEI

Titan G2, 300 kV) images.

In-situ K-O_2 nano battery setup in the ETEM

The nano battery was constructed through a two-probe configuration in a Cs-corrected ETEM (FEI, Titan G2, 300 kV). The α-MnO_2 NWs were used as the working cathode. They were glued to a half copper grid which was attached to an aluminum rod with conductive epoxy. Pure metal K scratched on an aluminum tip inside a glove box filled with argon gas (the oxygen and moisture content both below 0.01ppm) was used as the reference and counter electrode. The native K_2O layer formed on the surface of the K metal was used as a solid electrolyte for K^+ transportation. Both MnO_2 and K electrodes were mounted onto a TEM-STM (Scanning Tunneling Microscopy) holder (Pico Femto FE-F20 holder) inside a glove box. Then the holder was sealed in a home-built air-tight bag filled with dry argon and transferred to the TEM. The total time of exposure to the air was less than 2 s, which limited the extent of K_2O formation on the surface of the K metal. Prior to the experiment, high-purity O_2 (99.99%) was introduced to the specimen chamber with a pressure of 1.0 mbar. The α-MnO_2 NW was manipulated to approach the K_2O layer, and then a potential was applied to the NW versus the K metal electrode to discharge the NW.

2. Description of the Supplementary Movies

Movie S1. An in situ TEM movie showing the morphological evolution of the reaction product upon discharging of the K-O_2 battery, featuring the formation of KO_2 on the surface of a MnO_2 NW. The movie was compiled from TEM images which were acquired at about 1 frame/2 seconds, and is played at ~1000 × speed.

Movie S2. Another in situ TEM movie showing the morphological evolution of the reaction product upon discharging of the K-O_2 battery, featuring the formation of KO_2 on the surface of a MnO_2 NW. The movie was compiled from TEM images which were acquired at about 1 frame/2 seconds, and is played at ~400 × speed.

3. Supplementary Figures and Tables

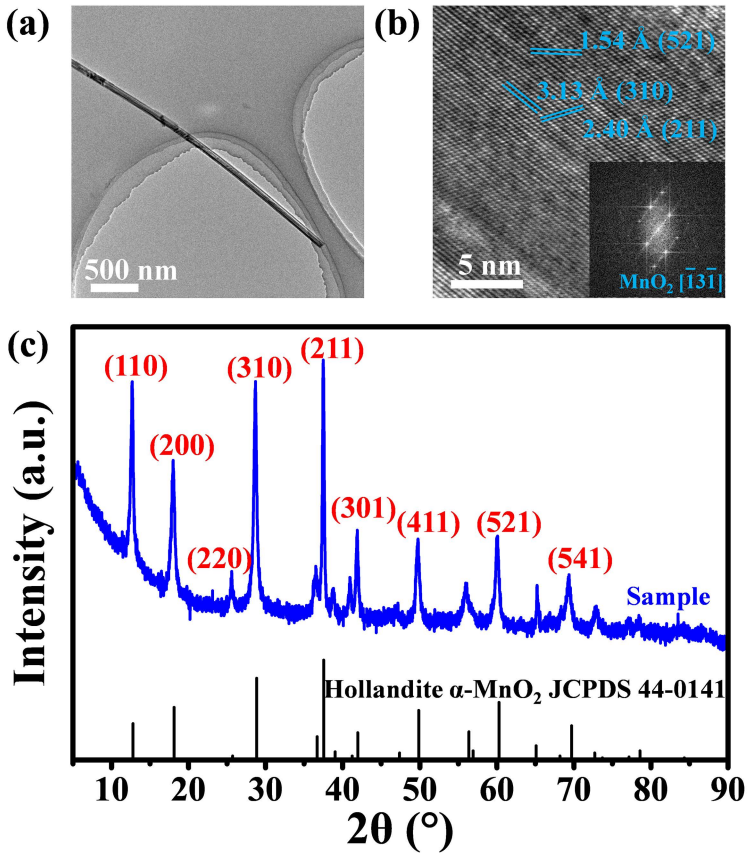

Fig. S1 (a) A TEM image of a single as-synthesized α-MnO_2 NW. (b) A high resolution TEM image of α-MnO_2. Inset is the corresponding FFT. (c) The XRD pattern of the as-synthesized α-MnO_2.

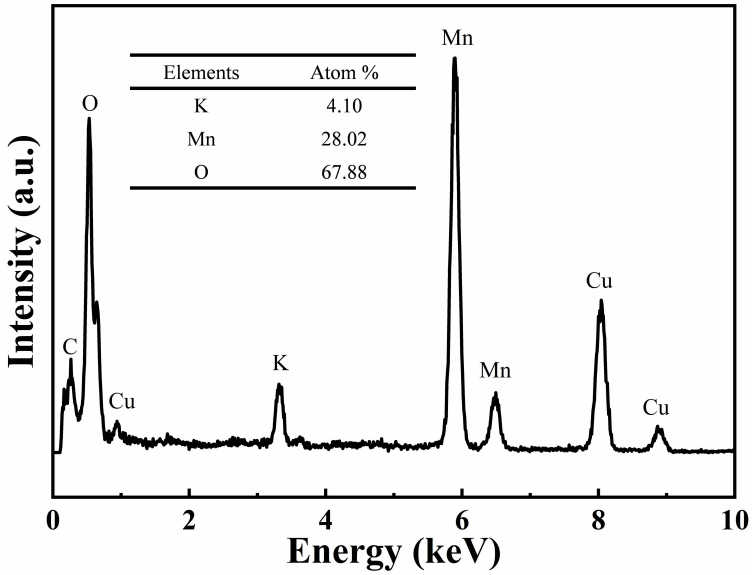

Fig. S2 The EDS characterization of the pristine α-MnO_2 nanowire. The element C and Cu is from the lacey carbon coated copper grid for the TEM test.

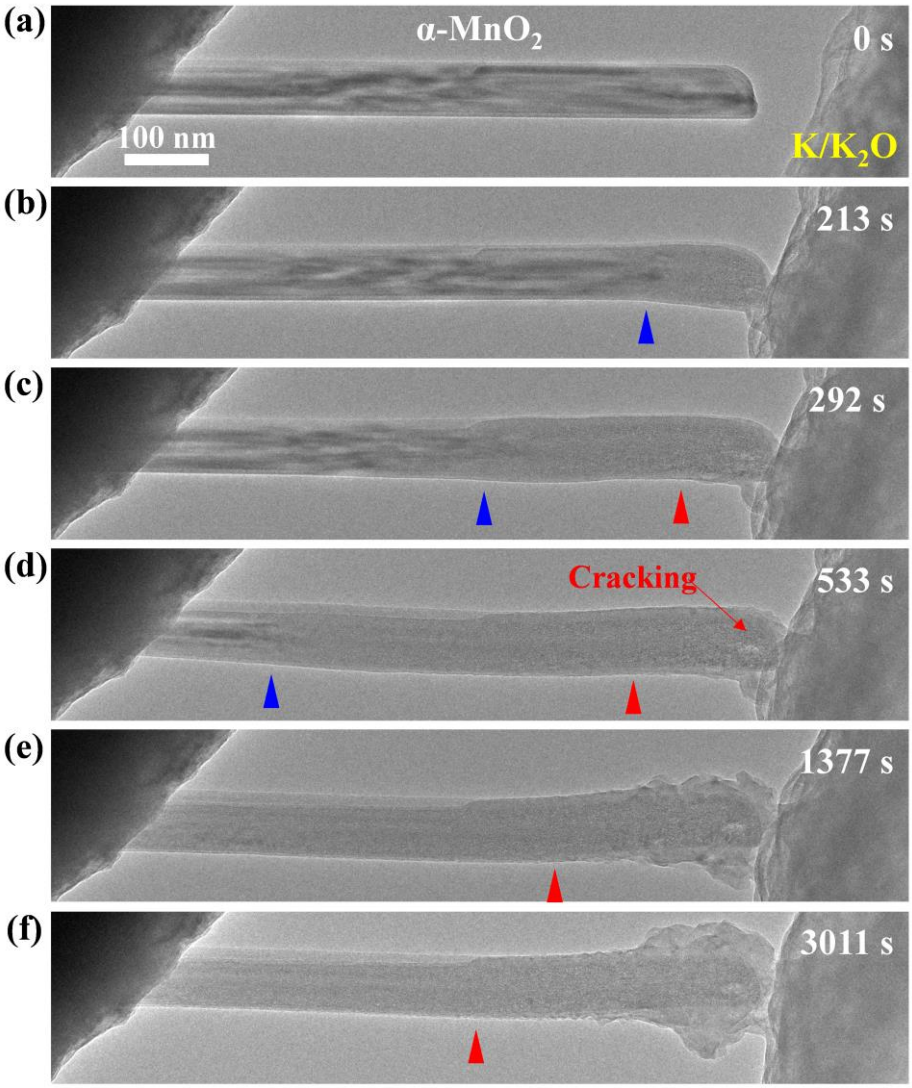

Fig. S3 (a-f) Time lapse TEM images showing the morphology evolution of α-MnO_2 NW during discharge with 1.0 mbar O_2. Blue and red arrowheads denote the first and second RFs, respectively.

Table S1 the Mn-L_3/L_2 data as measured by quantitative EELS analysis based on Fig. 3c.

Positions	**Pristine α-MnO_2**	**1**	**2**	**3**	**4**
Intensity ratio (L_3/L_2)	2.14	2.32	2.66	2.73	3.03
Estimated Mn oxidation state[a]	+3.4	+3.0	+2.7	+2.6	+2.3
Estimated Mn oxidation state[b]	+3.8	+3.2	+2.7	+2.6	+2.5

[a] Based on the reference 25 in the main text. (H. Tan, J. Verbeeck, A. Abakumov and G. Van Tendeloo, Ultramicroscopy, 2012, 116, 24–33.).

[b] Based on the reference 23 in the main text. (H. K. Schmid and W. Mader, Micron, 2006, 37, 426–432.).