

Supporting information for:

Oxide-on-Metal as an Inverted Design of Oxygen Electrocatalysts for Non-aqueous Li-O₂ Batteries

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1. Experiments

Synthesis of Ag-Mn₃O₄

1 mmol manganese nitrate Mn(NO₃)₂•4H₂O (Sigma Aldrich) and 0.1 mmol silver nitrate AgNO₃ (Merck) were dissolved in 20 mL ethylene glycol (EG, Sigma Aldrich). The resulting solution was stirred for 10 min at room temperature. 2 mmol anhydrous ethylene diamine (EN, Sigma Aldrich) was added to the solution dropwise with continued stirring; forming a grey precipitate gradually. The pH of the suspension at the end of addition was about 8-9. This suspension was transferred to a 50 mL Teflon-lined autoclave, sealed and heated at 180 °C for 6 h in an oven, and then cooled down to room temperature naturally. The grey solid product was filtered off, washed with ethanol for several times, and dried in an oven. The dried solid was then heat treated at 300 °C for 5 h in air in a tubular furnace to form Ag-Mn₃O₄ nanowheats.

Synthesis of Mn₃O₄

Mn₃O₄ was synthesized by a similar procedure without the addition of silver nitrate AgNO₃. 1 mmol manganese nitrate Mn(NO₃)₂•4H₂O was dissolved in 20 mL EG. 2 mmol anhydrous EN was added to the solution dropwise. After 10 min of stirring at room temperature, the mixture was transferred to a 50 mL Teflon-lined autoclave, sealed and heated at 180 °C for 6 h in an oven, and then cooled down to room temperature naturally. The solid product was filtered off, washed with ethanol several times, and dried in an oven. The dried solid was then calcined at 300°C for 5 h in air in a tubular furnace. The final product was coral-like aggregates of Mn₃O₄ nanoparticles (nanocorals).

Characterization

Powder XRD patterns were collected by a Bruker D8 Advance X-ray diffractometer with Cu K α radiation. A JEOL-JSM-6700F field-emission scanning electron microscope (FESEM) operating at 5 keV was used for morphology examination. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2010F. Energy-dispersive X-ray (EDX) measurements were carried out during the TEM sessions to determine average and local elemental compositions. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Kratos AXIS Hsi spectrometer using a monochromatic Al K α X-ray source. Fourier transform infrared spectra (FTIR) were recorded on a Shimadzu-8400 spectrophotometer using the KBr pellet method. The Ag and Mn contents of the samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo iCAP 7200).

Preparation of air cathodes for non-aqueous Li-O₂ cells

Air cathodes were prepared from a slurry of carbon black (Ketjen black EC 600JD, Shanghai Tengmin Corp.), polyvinylidene fluoride (PVDF, Sigma Aldrich), and Ag-Mn₃O₄ catalyst (in the weight ratio of 80:10:10) in N-methyl-2-pyrrolidone (NMP, Sigma Aldrich). The slurry was applied to a carbon paper (GasHub, Singapore) and dried at 100 °C overnight in vacuum. The catalyst loading in the composite cathode prepared as such was about 0.3 mg cm⁻². A catalyst-free electrode containing only carbon black (90 wt.%) and PVDF (10 wt.%) was also prepared for comparison.

Li-O₂ cell assembly and testing

The Li-O₂ test cell was a commercially available electrochemical cell (EQ-3ESTC15, MTI Corp.). Assembly was carried out in an Ar-filled glove box (H₂O < 1 ppm, O₂ < 1 ppm) using a lithium disc as the anode and Celgard 2400 as the separator. The electrolyte was 1 M lithium triflate (LiCF₃SO₃, Sigma Aldrich) in tetraethylene glycol dimethyl ether (TEGDME, Sigma Aldrich). The cell was rested for 6 h at room temperature to saturate the electrolyte with dissolved oxygen. The assembled cell was cycled galvanostatically by a Neware BTS-5V-1mA battery tester in the voltage range of 3.8 to 2.3 V (vs. Li⁺/Li) at two current densities: 0.02 and 0.05 mA cm⁻². All the tests were

conducted under 1 atm pressure of O_2 at room temperature. Specific capacities were calculated using the total weight of the oxygen cathode (including the weights of binder, catalyst and carbon black).

2. Supporting Figures

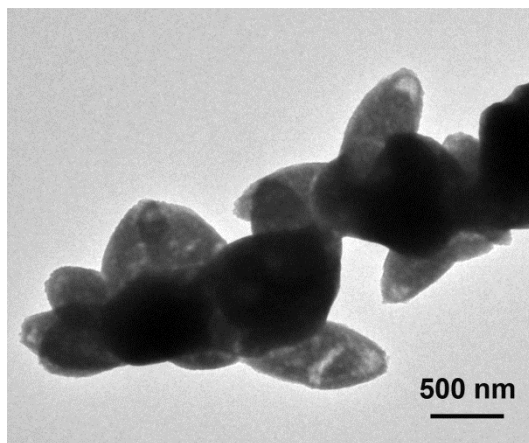


Fig. S1 TEM image of the as-prepared Ag-Mn₃O₄ catalyst.

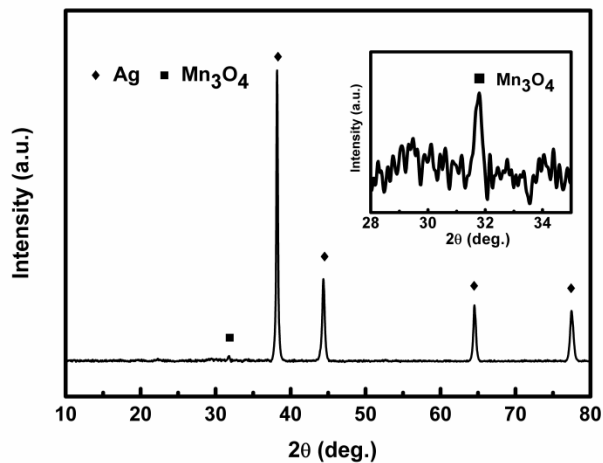


Fig. S2 XRD pattern of the as-prepared catalyst. Mn₃O₄ JCPDS No. 75-1560, Ag JCPDS No. 03-0931. (inset: enlarged Mn₃O₄ peak).

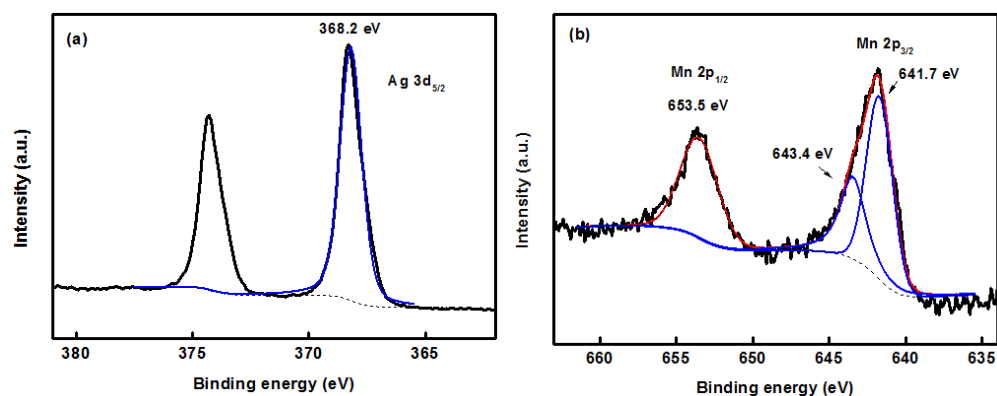


Fig. S3 XPS spectra of the as-prepared Ag-Mn₃O₄ catalyst: (a) in the Ag 3d region (b) in the Mn 2p region. The XPS peaks were corrected for C 1s of adventitious carbon at 284.6 eV. The Mn 2p_{3/2} spectrum could be deconvoluted as two pairs of doublets (blue lines). The 641.7 eV peak is attributed to the Mn 2p_{3/2} of Mn(II) (as in MnO), and the 643.4 eV peak is the Mn 2p_{3/2} of Mn(IV) (as in MnO₂). The area ratio of these two peaks was about 2:1, consistent with the theoretical stoichiometry of Mn₃O₄ as 2MnO•MnO₂. (The dashed line is the background; the red line is for the fitted peak).

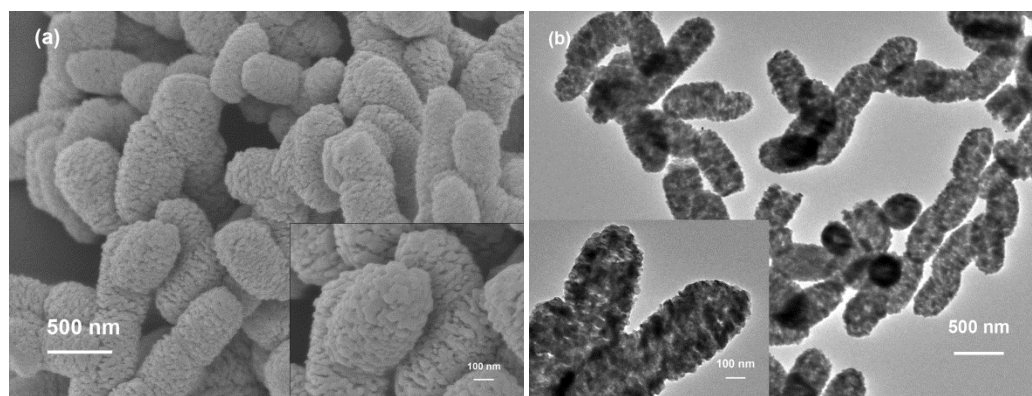


Fig S4. (a) FESEM images of Mn₃O₄ nanocorals (inset: a high-magnification FESEM image); (b) TEM images of Mn₃O₄ nanocorals (inset: a high-magnification TEM image). Without AgNO₃, Mn₃O₄ was formed under similar synthesis conditions. The Mn₃O₄ nanoparticles aggregated to form a coral-like structure (nanocorals) with size of ~300 nm.

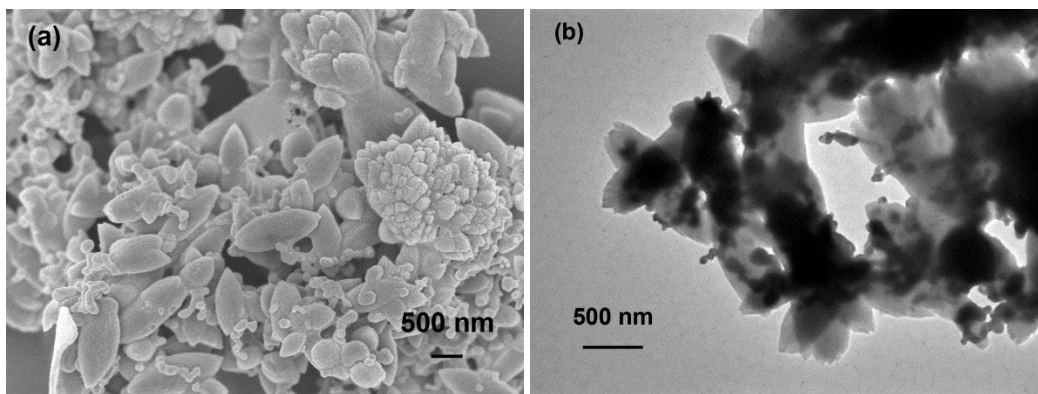


Fig S5. FESEM (a) and TEM (b) images of Ag-Mn₃O₄ composites prepared by NaOH addition instead of EN addition. The surface of Ag seeds provided as the heterogeneous nucleation sites for the confined growth of MnCO₃. No free Mn₃O₄ or Ag nanoparticles were found in the reaction system after the reaction. When NaOH, a strong base, was used in lieu of EN in the synthesis (while keeping all other conditions the same), the product was a mixture of Ag and Mn₃O₄ and not an intimately integrated hybrid system. Random distribution of Ag with various particle sizes in the mixture was found, although Mn₃O₄ were all morphologically similar.

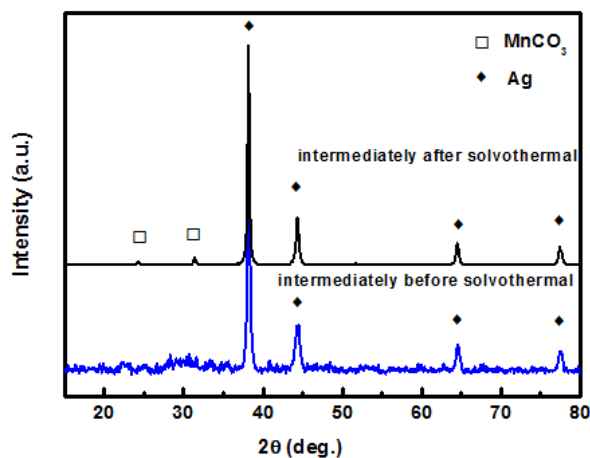


Fig. S6. XRD patterns of the reaction mixture before and after solvothermal treatment (Ag JCPDS No. 03-0931, MnCO₃ JCPDS No. 44-1472).

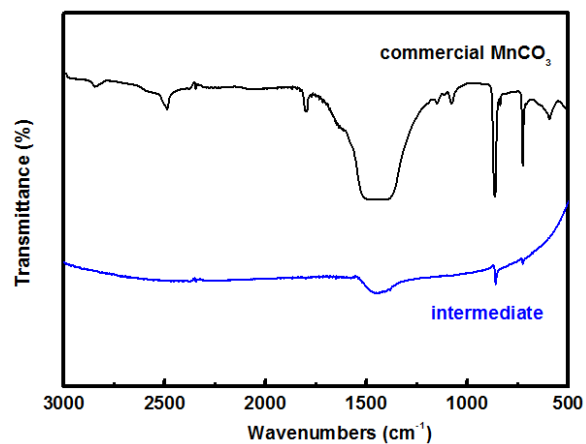


Fig. S7 FTIR spectra of commercial MnCO₃ and of the intermediate product from the solvothermal reaction. The characteristic peaks at 1448 and 862 cm⁻¹ are in agreement with the CO₃²⁻ vibrations of a commercial MnCO₃ sample.

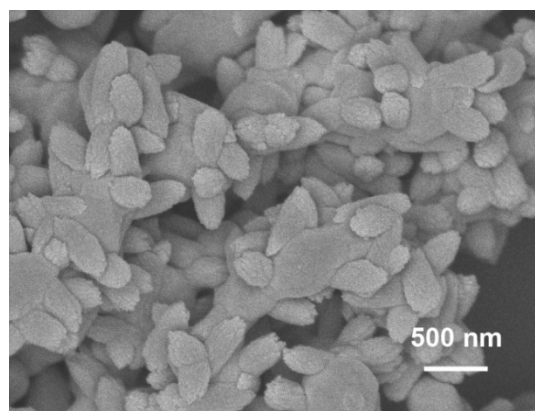


Fig. S8 FESEM image of the product of solvothermal reaction (before heat treatment).