Electronic Supplementary Information

Synthesis of Octahedral Mn_3O_4 Crystals and Their Derived Mn_3O_4-MnO_2 Heterostructures via Oriented Growth

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Experimental

All chemicals were purchased from Aldrich and used as received without further purification.

Synthesis of Mn_3O_4 nanostructures. In a typical hydrothermal synthesis, 0.694 g of $KMnO_4$ and 1.0 mL of ethylene glycol were added to 40 mL of deionized water under magnetic stirring to form the precursory suspension. After stirring for about 20 min, the suspension was transferred into a Teflon-lined stainless steel autoclave with a capacity of 70 mL. The autoclave was then heated in an electric oven at different temperatures (100 – 200 ^oC) for 12 h. After the autoclave was cooled down naturally to room temperature, the khaki precipitate was harvested by centrifugation and washed with deionized water for 3 times and acetone once before room temperature vacuum drying.

Synthesis of birnessite-MnO_2/Mn_3O_4 core-shell structures. The birnessite-MnO_2/Mn_3O_4 core-shell structures were fabricated by a facile seed-epitaxial route employing synthesized Mn_3O_4 nanostructures as seeds. Typically, 0.10 g of synthesized Mn_3O_4 seeds, 0.25 g of $KMnO_4$ and 0.8 mmol of HCl were ultrasonically dispersed into 50 mL of deionized water to form the precursory suspension in a sealed glassy vial. The vial was then heated to 95 °C in an oil bath for different durations under magnetically stirring. After the vial was cooled down naturally to room temperature, brown precipitate was harvested by centrifugation and washed with deionized water for 3 times and acetone once before room temperature vacuum drying.

Materials characterization. Crystallographic information of all as-prepared samples was investigated with X-ray powder diffraction (XRD; Bruker, D8-Advance X-ray Diffractometer, Cu Kα, λ = 1.5406 Å) at a scan rate of 1° min^{-1}. The morphology of as prepared samples was examined with field-emission scanning electron microscopy (FESEM; JSM-6700F) and high-resolution analytical transmission electron microscopy (TEM, JEM-2010, 200 kV; HRTEM, Philips FEG CM300, 300 kV) with Selected Area Electron Diffraction (SAED) capability.

Electrochemical characterization. The electrochemical measurements on lithium storage capability were carried out using two-electrode Swagelok-type cells with lithium metal as the counter and reference electrodes at room temperature. The working electrode consists of 80 wt% of the active material (e.g., Mn_3O_4 octahedra), 10 wt% of conductivity agent (carbon black, Super-P-Li), and 10 wt% of binder (polyvinylidene difluoride, PVDF, Aldrich). The electrolyte is 1 M $LiPF_6$ in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an Ar-filled glove box with the concentrations of moisture and oxygen below 1 ppm. Cyclic voltammetry and galvanostatic charge/discharge cycling were carried out with an electrochemical workstation (CHI 660C) and a battery tester (Shenzhen Neware), respectively.

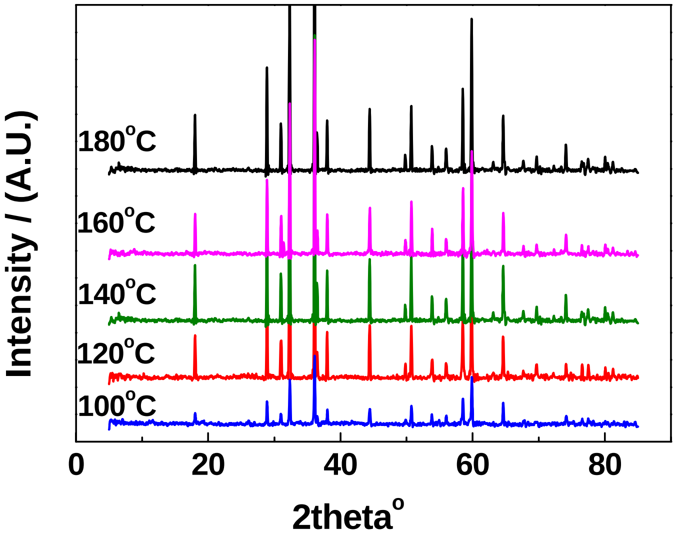

Figure S1. XRD patterns of Mn_3O_4 prepared for 12 h at different temperatures. All patterns can be well indexed to tetragonal hausmannite-Mn_3O_4 (JCPDS: 24-0734, $I4_1/amd$, $a = b = 5.76$ Å, $c = 9.47$ Å) and no other impurities can be observed, which indicates the highly phase purity of product.

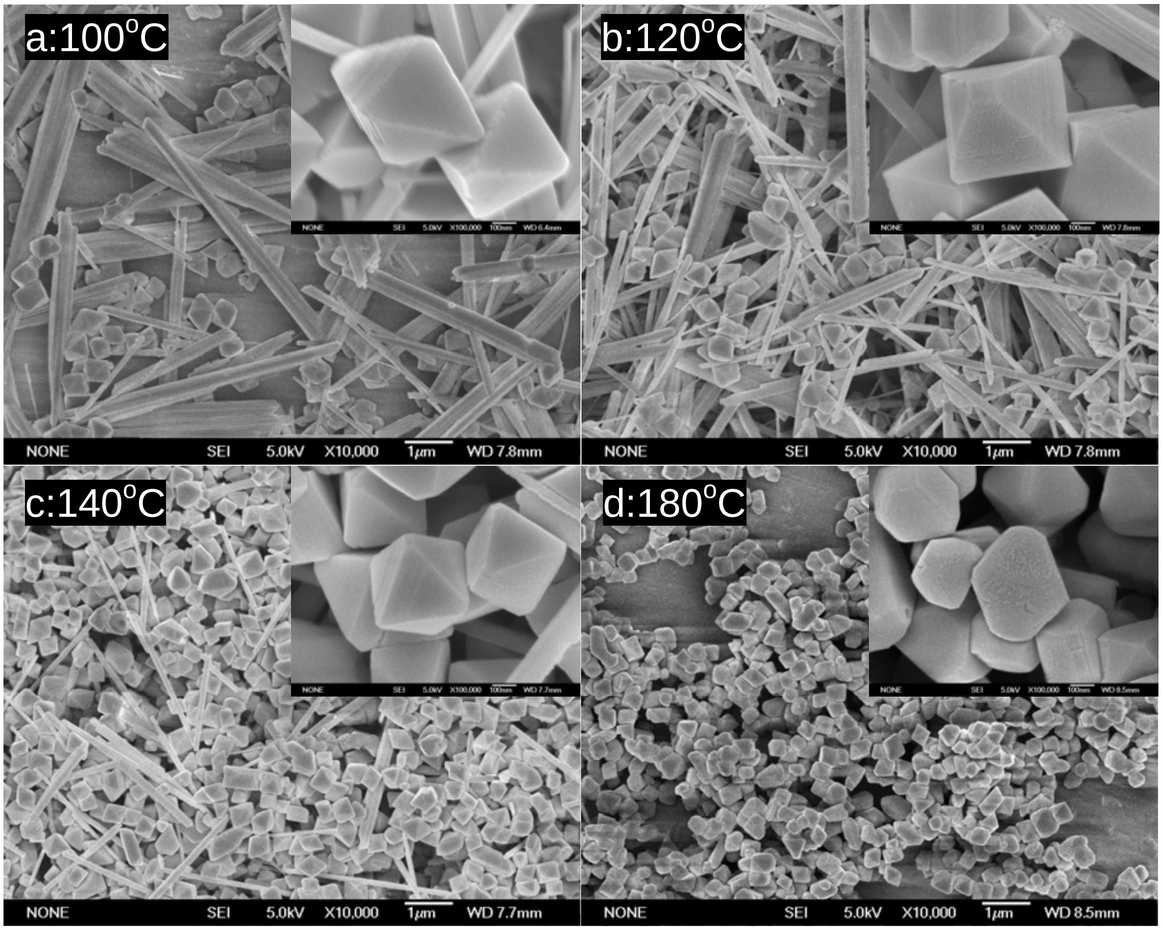

Figure S2. SEM images of Mn_3O_4 prepared for 12 h at 100 °C (a), 120 °C (b), 140 °C (c) and 180 °C (d). The insets show the corresponding high-magnification SEM images.

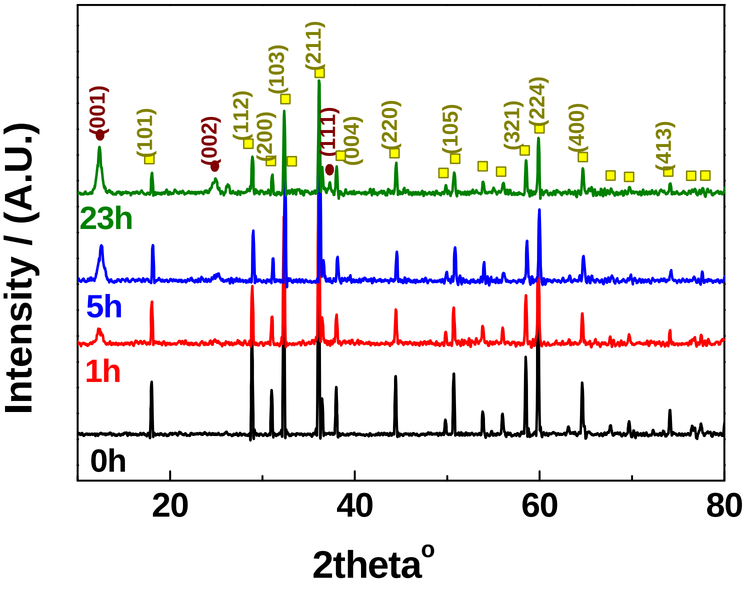

Figure S3. XRD patterns of Mn_3O_4 octahedra prepared at 160 °C for 12 h before and after reaction with acidic $KMnO_4$ aqueous solution at 95 °C for 1 h, 5 h and 23 h. The patterns show that the product transforms from intrinsic hausmannite-Mn_3O_4 (denoted as yellow squares) to the mixture of Mn_3O_4 and birnessite-MnO_2 (denoted as brown circles, JCPDS No. 80-1098, monoclinic, *C2/m*, a = 5.15 Å, b = 2.84 Å, c = 7.17 Å) after reaction.

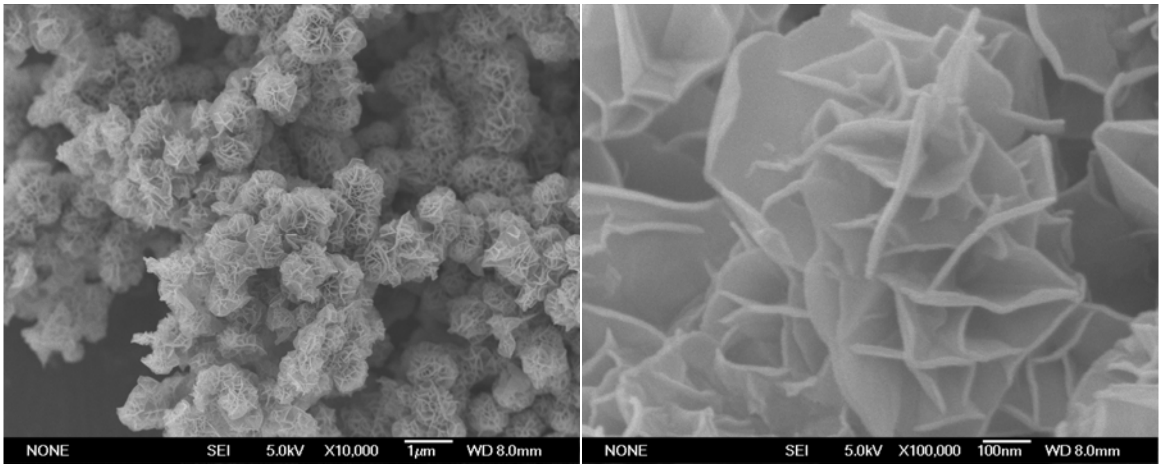

Figure S4. SEM images of product hydrothermally prepared at 95 °C for 12 h of acidic $KMnO_4$ aqueous solution (0.25 g of $KMnO_4$ and 0.8 mmol of HCl were ultrasonically dispersed into 50 mL of deionized water).

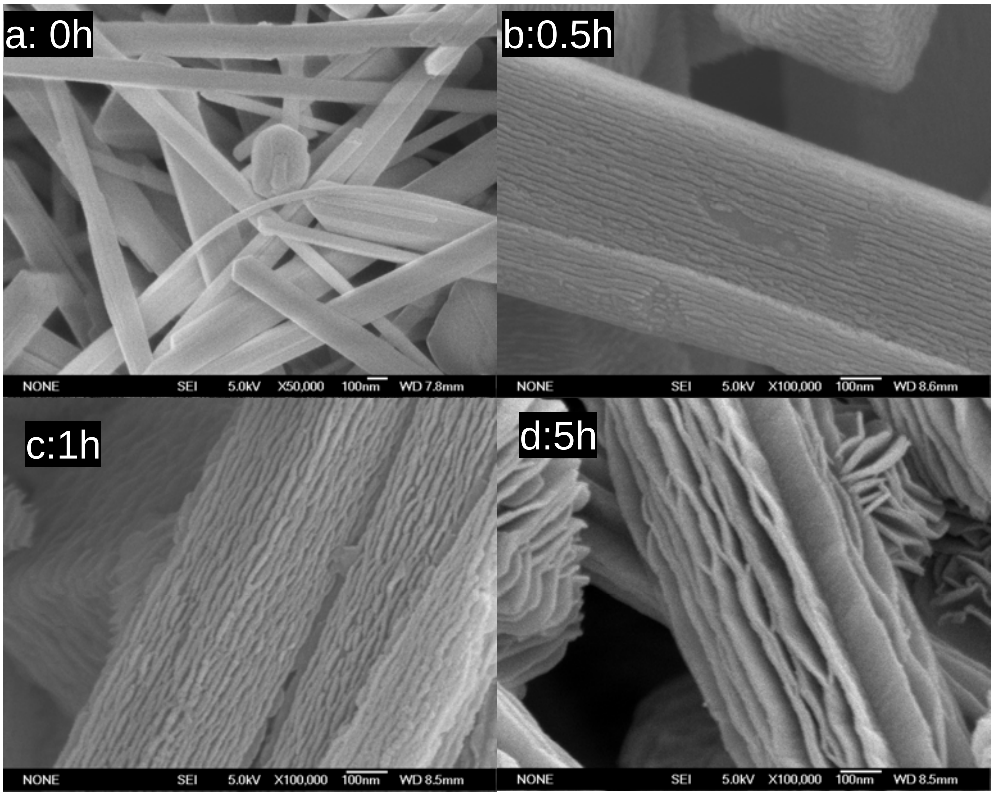

Figure S5. High-magnification SEM images of Mn_3O_4 prepared at 120 °C for 12 h (the product is mixture of octahedral and nanorods) after reaction with acidic $KMnO_4$ aqueous solution at 95 °C for 0 h (a), 0.5 h (b), 1 h (c) and 5 h (d).

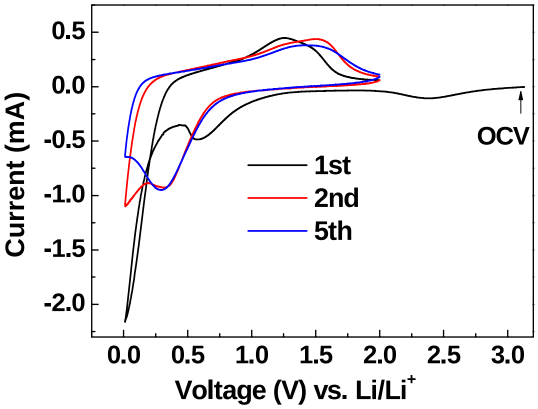

Figure S6. Cyclic voltammograms with a scan rate of 0.2 mV s^{-1}.