

Electronic Supplementary Information

Single-Unit-Cell Thick Mn_3O_4 Sheets

Hongwen Huang, Qing Yu, Xinsheng Peng,* Zhizhen Ye

State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering,
Zhejiang University

1 Experimental Section

Synthesis of single-unit-cell thick Mn_3O_4 nanosheets, $\text{Mn}(\text{OOH})$ nanofibers and Mn_3O_4 nanoparticles:

Mn_3O_4 nanosheets were typically synthesized as: after purging 10 ml 0.4 mM $\text{Mn}(\text{NO}_3)_2$ solution and 10 ml 0.8 mM aminoethanol (AE) solution by pure argon for 30 mins, respectively, then AE solution was injected into the $\text{Mn}(\text{NO}_3)_2$ solution under stirring. The argon stream was kept for 3 hours. After reaction for one day, the grey-brown suspensions were collected by filtered on a polycarbonate membrane with 200 nm pores. Simply replace the argon with pure oxygen, MnOOH nanofibers were obtained. Similar to the synthesis process of Mn_3O_4 nanosheet, Mn_3O_4 nanoparticles were prepared by using KOH as the basic source and keep the other conditions the same.

Characterization: The morphologies and structures of the films were characterized by using a SEM (*Hitachi S-4800*). SEM observation was conducted after coating a 2 nm thick platinum layer by using a *Hitachi e-1030* ion sputter at the pressure of 10 Pa and the current density of 10 mA. The TEM and HRTEM images were recorded by JEOL 2100F. X-ray diffraction patterns were performed by X'Pert PRO (PANalytical, Netherlands). XPS spectra were measured by ESCALAB 250 X-ray photoelectron spectroscopy. Raman spectroscopy was recorded by Labor Raman HR-800 equipment (Jobin Yvon, France). Laser excitation is 514.5 nm. The power is 10 mW with integration time of 10 seconds. The magnetic of the as-synthesized Mn_3O_4 nanosheets were investigated by a SQUID magnetometer (Quantum Design).

2 AFM characterization of the as-synthesized sheets

For AFM measurement, after sonicating the collected nanosheets in ethanol for 10 mins, a small drop of the dispersion was spin-coated on a highly ordered pyrolytic graphite (HOPG) surface. The measurements were carried out using tapping mode (Veeco Multimode) . Figure S1 shows the AFM image and the thickness along the marked line in the image. It is clear that the thickness of the nanosheet is about 1.05 nm.

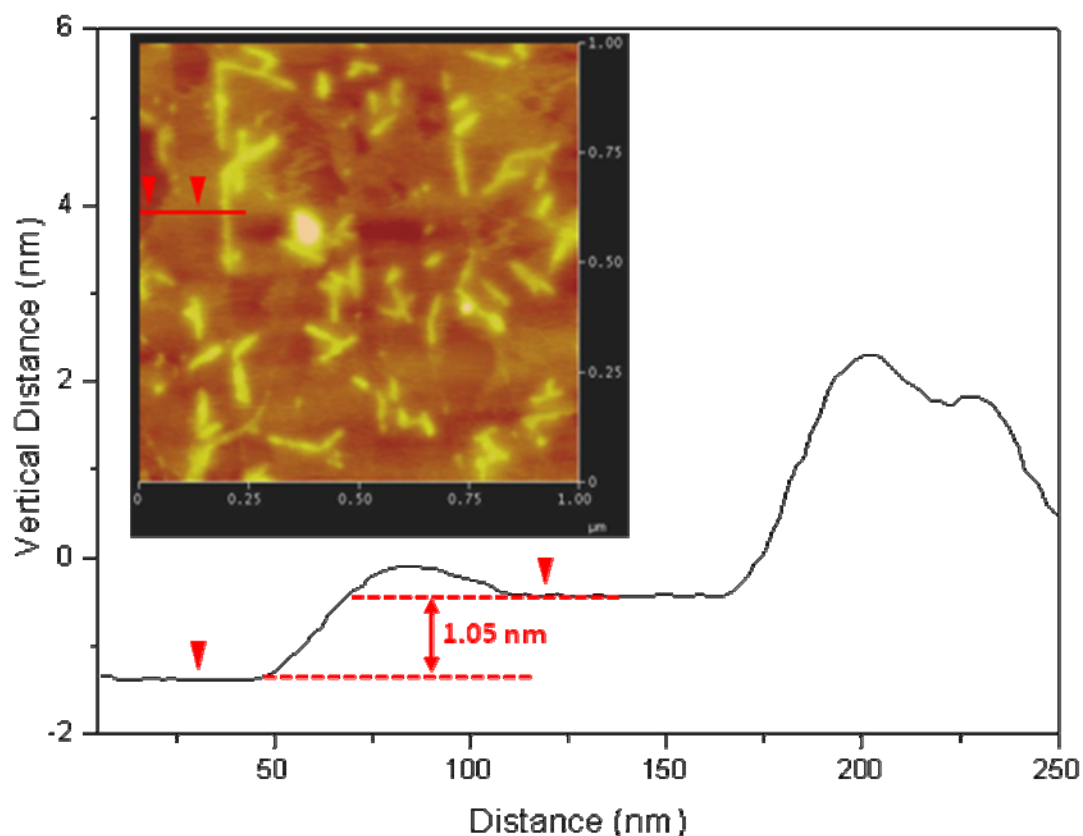


Figure S1 AFM image and thickness plot of the as-synthesized nanosheets.

2 Formation and characterization β -MnOOH nanofibers synthesized by purging oxygen

For comparison, the oxygen purging process was utilized in place of argon, while all the process remained the same (10 ml, 0.4 mM $\text{Mn}(\text{NO}_3)_2$ and 10 ml, 0.8 mM AE). It was found that nanofibrous structures were formed as shown in Figure S2, after 12 hours, when purging oxygen through the reaction solution with a 100 sccm flow rate. The corresponding XRD indicates that these nanofibers are in the phase of β -MnOOH,¹ and the same as β -MnOOH nanofibers that were synthesized at room temperature in air (ref. 11 in the main text). This means that the oxygen amount plays a key role in the formation of

Mn₃O₄. At higher oxygen concentrations, with the continuous purging of oxygen, the Mn²⁺ ions were completely oxidized to Mn³⁺ and formed β-MnOOH nanofibers. It is not energy available to transition to much higher valent manganese ions.¹ At low oxygen concentration, the Mn²⁺ was partially oxidized to Mn³⁺ and formed Mn₃O₄ by reconstructed the remaining Mn²⁺.

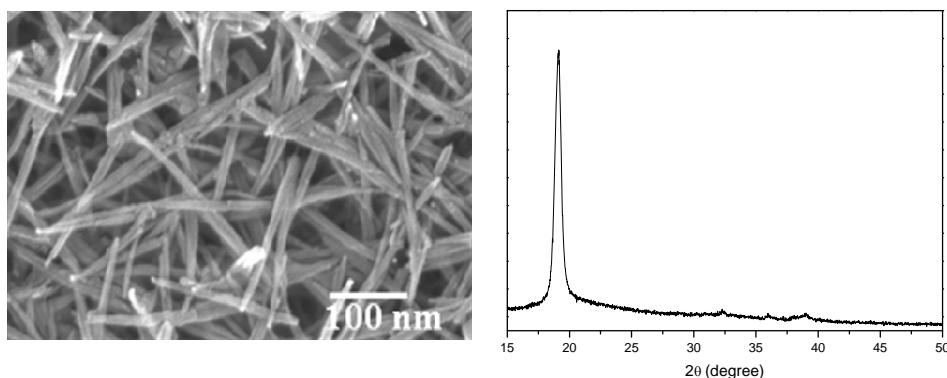


Figure S2 SEM image and XRD of the sample prepared by purging oxygen.

3 Formation Mn₃O₄ nanoparticles by using KOH replace aminoethanol

Figure S3 shows a SEM image of the sample prepared via the mixture of 10 ml 0.4 mM Mn(NO₃)₂ solution and 10 ml 0.8 KOH solution. Before mixing, the solutions were purged by pure argon for 30 mins, respectively. Then the KOH solution was injected into the Mn(NO₃)₂ solution under stirring. The argon stream was maintained for three hours. The reaction was elongated for 24 hrs. It is clearly seen that nanoparticles with diameter of 40-60 nm were formed and absent of sheet structures. The XRD results demonstrated that the phase of the nanoparticle is distorted spinel Mn₃O₄ (JCPDF 24-0734).

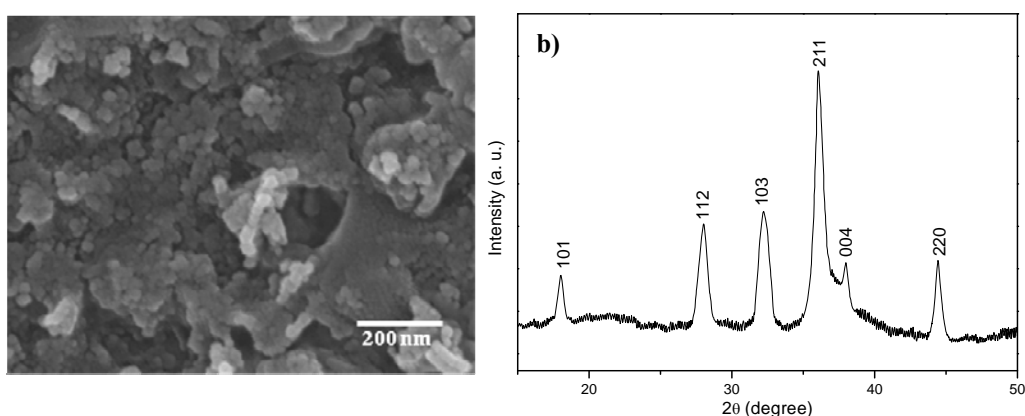
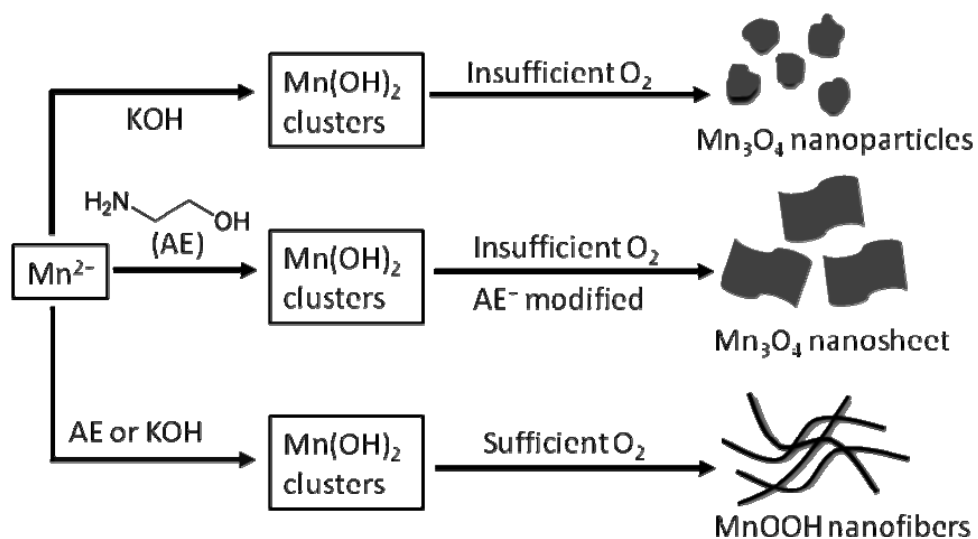


Figure S3 (a) SEM image and (b) XRD pattern of Mn₃O₄ nanoparticles prepared from 0.4 mM Mn(NO₃)₂ and 0.8 mM KOH.

4 Schematic diagram of the formation mechanism of the manganese oxide or hydroxide nanostructures at room temperature



Scheme S1 Illustration of the formation processes of different manganese oxide or hydroxide phases.

5 Raman and X-ray photoelectron spectroscopy spectra

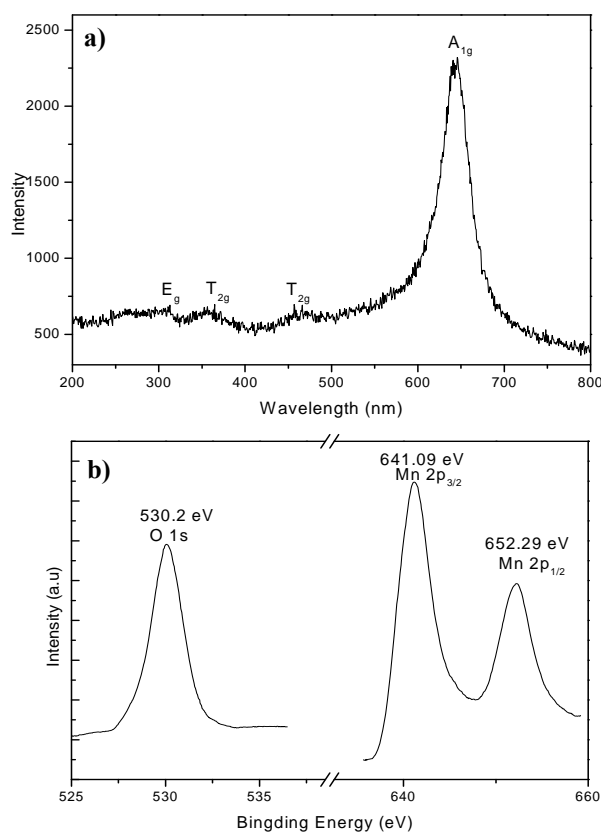


Figure S4 (a) Raman and (b) XPS spectra recorded from the as-synthesized sheets.

Reference:

1. K. W. Mandernack, J. Post, B. M. Tebo, *Geochim. Cosmochim. Acta* 1995, 59, 4393.