Self-Assembly of Birnessite Nanoflowers by Staged Three-Dimensional Oriented Attachment

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SI Supporting material and methods

S1. High-energy X-ray total scattering. Synchrotron Synchrotron-based X-ray total scattering data were collected using an X-ray of 58.6491 keV (λ = 0.2114 Å) at beamline 11-ID-B of the Advanced Photon Source (APS), Argonne National Laboratory (APS). The measurement was performed using the rapid acquisition PDF method by employing a Perkin Elmer amorphous silicon detector. The image plate was exposed for 1 s and the measurement was repeated 120 times for a total collection time of 120 s for each sample. The software Fit2D was used to integrate and convert the 2-D raw data to 1-D intensity versus wave vector (*Q*) data. The PDF, G(r), was obtained from the raw 1-D data using the program PDFgetX2.

S2. X-ray photoelectron spectroscopy. X-ray photoelectron spectra were collected using a VG Multilab2000 X-ray photoelectron spectrometer with an Al K X-ray source (1486 eV) and a base pressure of 3×10^{-9} Torr in the analytical chamber. The scans were recorded using the large area mode. The survey scans were collected using a fixed pass energy of 100 eV and an energy step size of 1.0 eV, whereas the narrow scans have a pass energy of 25 eV and an energy step size of 0.1 eV. The charge effect was corrected by adjusting the binding energy (BE) of C (1s) to 284.62 eV. The spectra were analyzed using the Avantage software. The Shirley-type background was subtracted before deconvolution and fitting. The parameters used by Nesbitt et al for the multiplet peaks of Mn ($2p_{3/2}$) for spectra fitting were adopted. A 20:80 ratio of the Lorentzian: Gaussian mix-sum function was used for all the fittings.

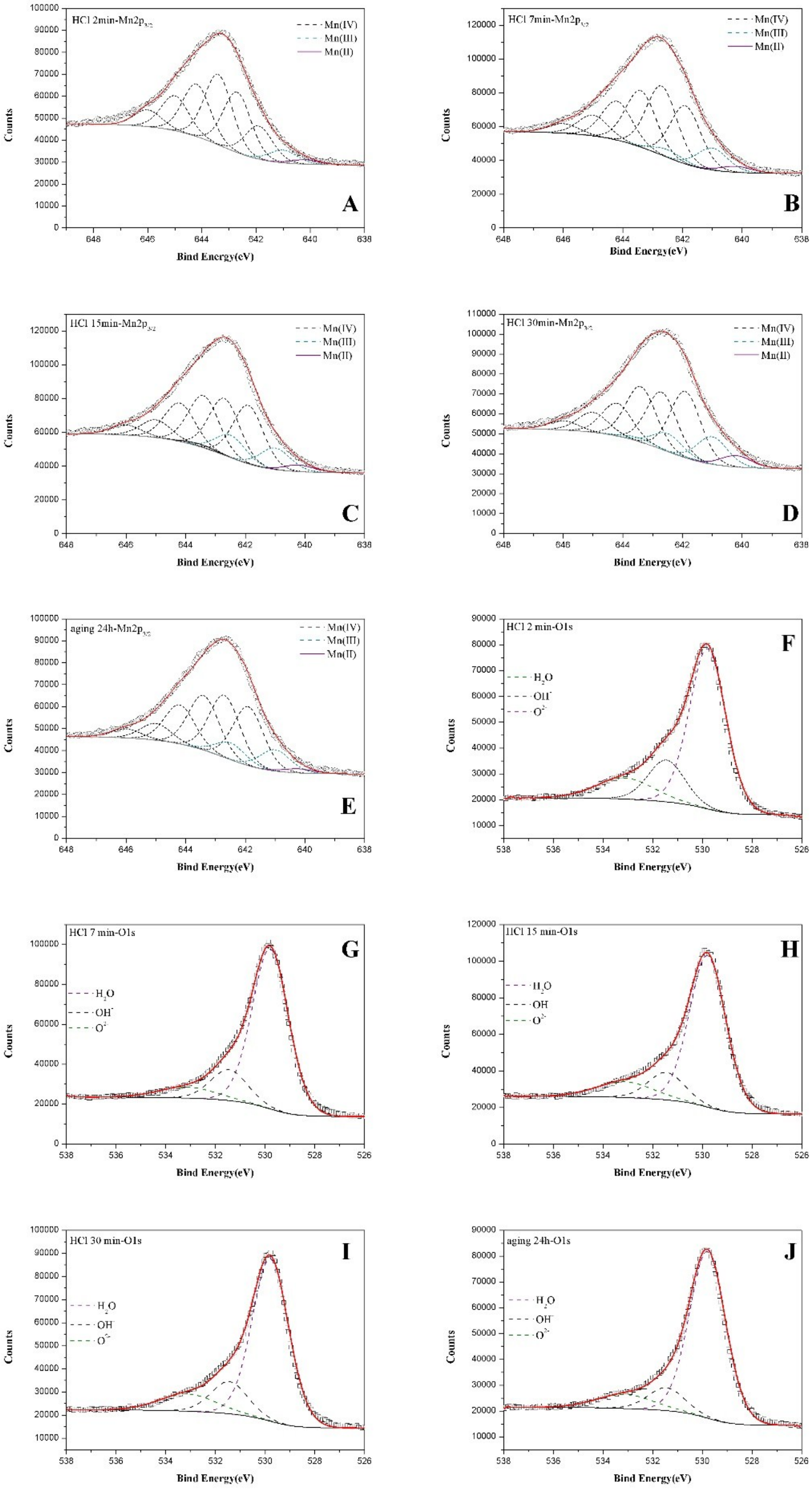

Fig. S1 XPS broad scans of Mn 2p$_{3/2}$ spectra of intermediate products at HCl 2min, 7min, 15 min, 30min and aging 24 h (A to E). And the O1s spectra of intermediate products at HCl 2min, 7min, 15 min, 30min and aging 24 h show in image F to L.

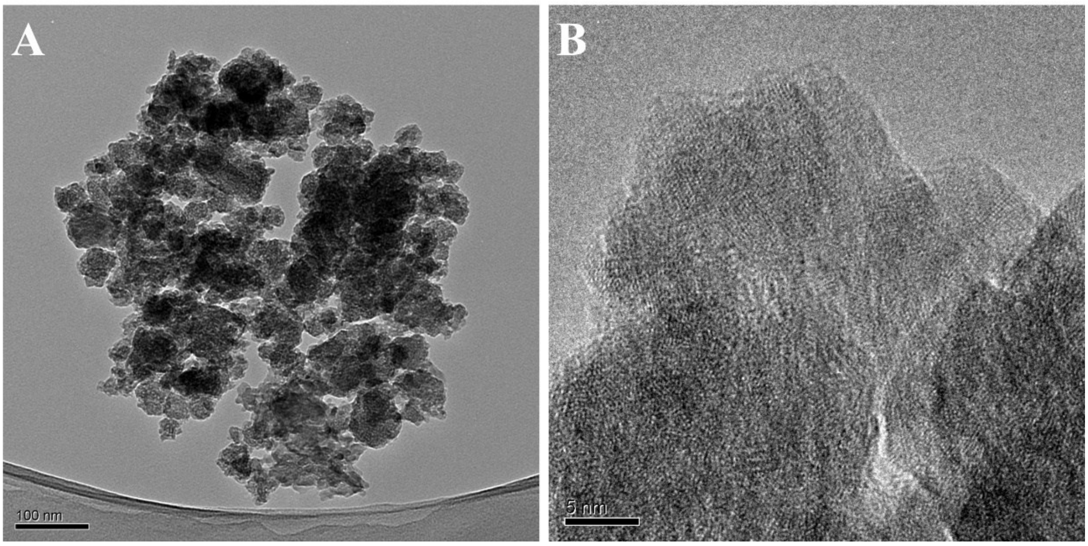

Fig. S2 TEM (A) image of the primary particles formed at 2 min of HCl addition. HRTEM image (B) of the primary paticles.

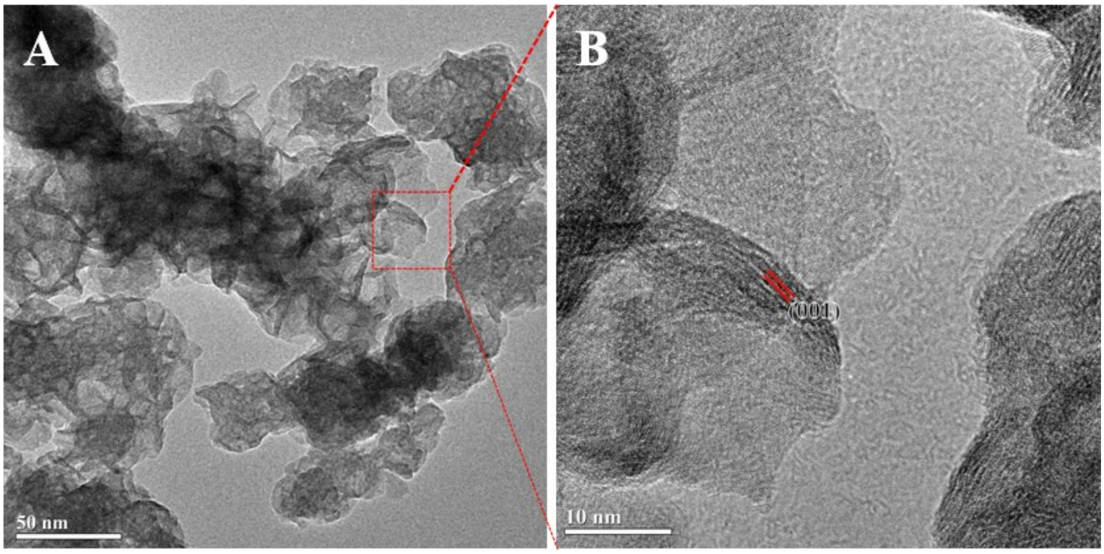

Fig. S3 TEM (A) image of the intermediate nanoflowers formed at 7 min of HCl addition. Image B is HRTEM image in the region of red area outlined in image A. The corresponding birnessite *d*-spacing indicated by the red parallel lines.

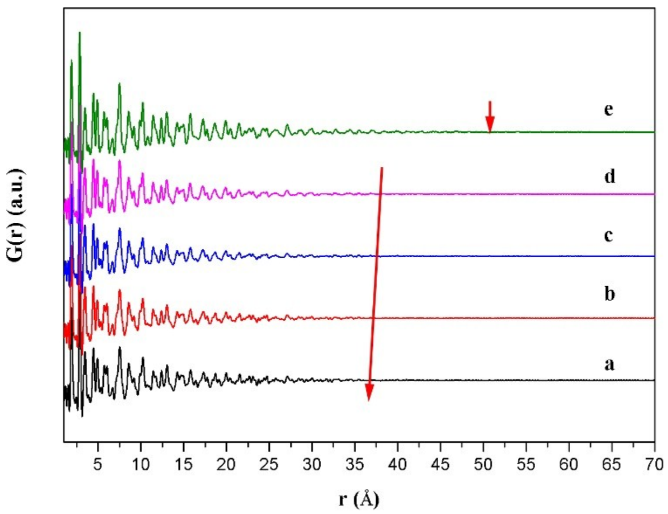

Fig. S4 Pair distribution function [G(r)] of intermediate products at different intervals of birnessite formation and crystal growth: (a) HCl, 2 min; (b) HCl, 7 min; (c) HCl, 15 min; (d) HCl, 30 min; and (e) aging 24 h with the r range of 1-70Å.

Table S1. Estimation of Thicknesses in the stacking direction based on (001) diffraction peaks using the scherer equation and the d-spacing of (100) and (110) peaks of intermediate products

Samples	Thickness $_{001}$ (nm)	d_{100} (Å)	d_{110} (Å)
HCl 2min		2.459	1.426
HCl 7min	4.09	2.440	1.416
HCl 15min	4.35	2.436	1.416
HCl 30min	5.70	2.436	1.413
aging 24h	7.30	2.436	1.413

Table S2. Concentration of $KMnO_4$ and pH in solution at various time intervals during birnessite formation process.

	Concentration of $KMnO_4$ mol/L	pH
HCl 2min	0.381	1.21
HCl 7min	0.354	0.83
HCl 15min	0.298	0.79
HCl 30min	0.195	0.72
60 aging 24h	0.190	0.78