Supplementary Information

Low-Temperature Fabrication of Crystalline MnCoO Spinel Film on Porous Carbon Paper for Efficient Oxygen Evolution Reaction

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Experimental

Synthesis and exfoliation of alpha $Co(OH)_2$

The alpha form of layered cobalt hydroxide was synthesized by slow hydrolysis of hexamethylenetetramine (HMT) with $CoCl_2 \cdot 6H_2O$, NaCl. A 0.5 g of solid green product was dispersed in 1.0 L of formamide by continuously stirring at 60 °C until the colloidal solution became transparent and red, indicating a successful exfoliation of the pristine alpha cobalt hydroxide, denoted as $Co(OH)_2$ nanosheet.

Synthesis of MnCoO spinel film on CFP substrate

The CFP substrates were first cleaned by immersing them in ethanol in an ultrasonic bath for 5 min, and then purged with nitrogen gas. A 1×7 cm^2 piece of CFP substrate and a 30 mL of an aqueous solution containing 5 mM mixture of $MnCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$, 5 mM HMT, and 0.3 mL $Co(OH)_2$ nanosheet solution (0.5 g/L) were transferred into a 50 mL Teflon-lined autoclave reactor. The mixture was heated at around 120 °C for 6 h. The MnCoO/CFP substrates were washed with deionized water and ethanol several times and dried nitrogen gas. Control experiments without $Co(OH)_2$ nanosheet solution under the same reaction condition produced a mixture of $Co(OH)_2$ microparticle and MnCoO particles. Synthesis of pure MnCoO nanoparticles yielded ~30 mg/100 mL solution.

Electrochemical measurements

Electrochemical studies were carried out in a standard three-electrode system controlled by a CompactStat system (Ivium Technologies) with MnCoO coated CFP substrate as the working electrode, Pt plate having 1×7 cm^2 of surface area as the counter electrode, and saturated Ag/AgCl electrode as the reference electrode, respectively. The electrochemical impedance spectroscopy (EIS) test was carried out in the same three-electrode cell in 1 M KOH. Impedance data was recorded at 0.6 V vs Ag/AgCl. The data were collected in the frequency range of 100,000 ~ 1 Hz with a 5 mV amplitude. All the tests were performed at room

temperature.

General Characterization

SEM images and EDX data were recorded using a Field Emission Scanning Electron Microscope (JSM-7800F Prime, JEOL Ltd.). HR-TEM image was taken using JEM-3010 (JEOL). XRD data were generated using a Miniflex 600 X-ray diffractometer (Rigaku) with Cu_{Ka} radiation at l = 1.5405 Å. X-ray photoelectron spectroscopy (XPS) was achieved through an ESCALAB 250 (Thermo Scientific).

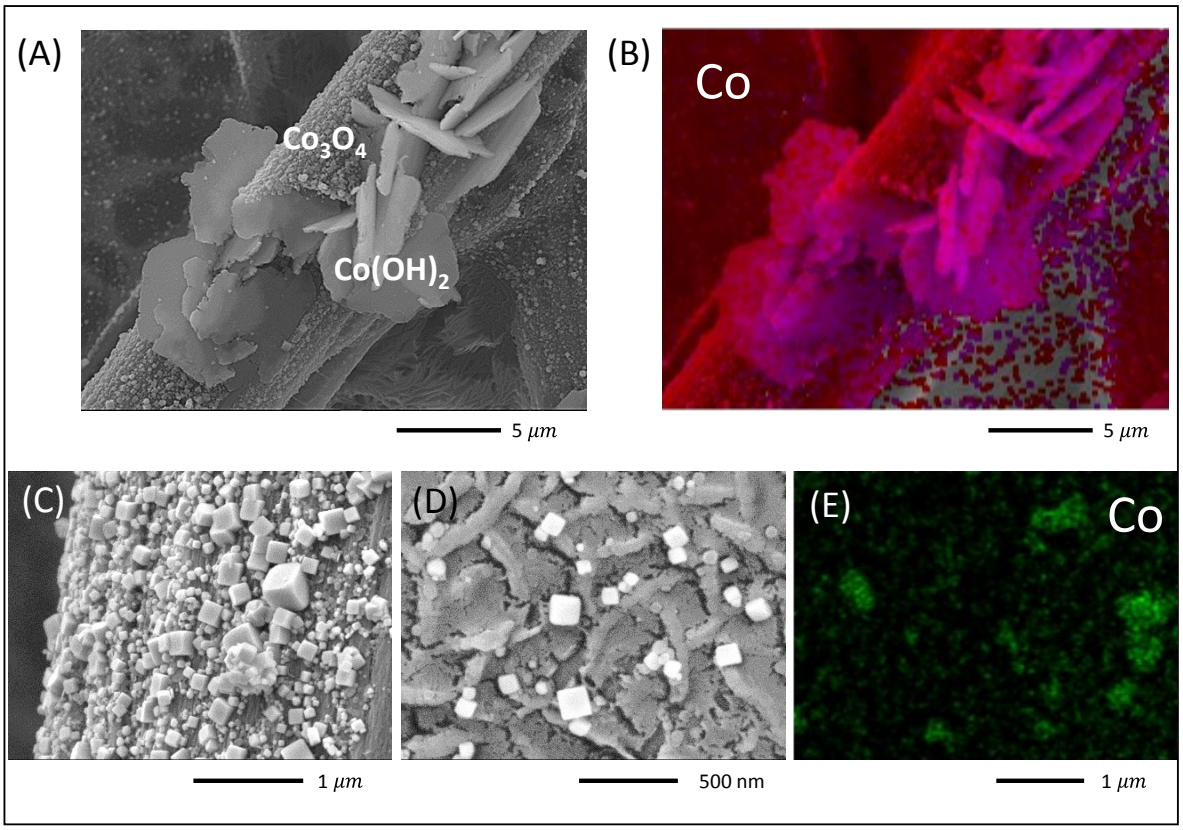

Figure S1. (A, C, D) SEM images and (B, E) elemental map (Co) of Co_3O_4/CFP prepared by the hydrothermal method.

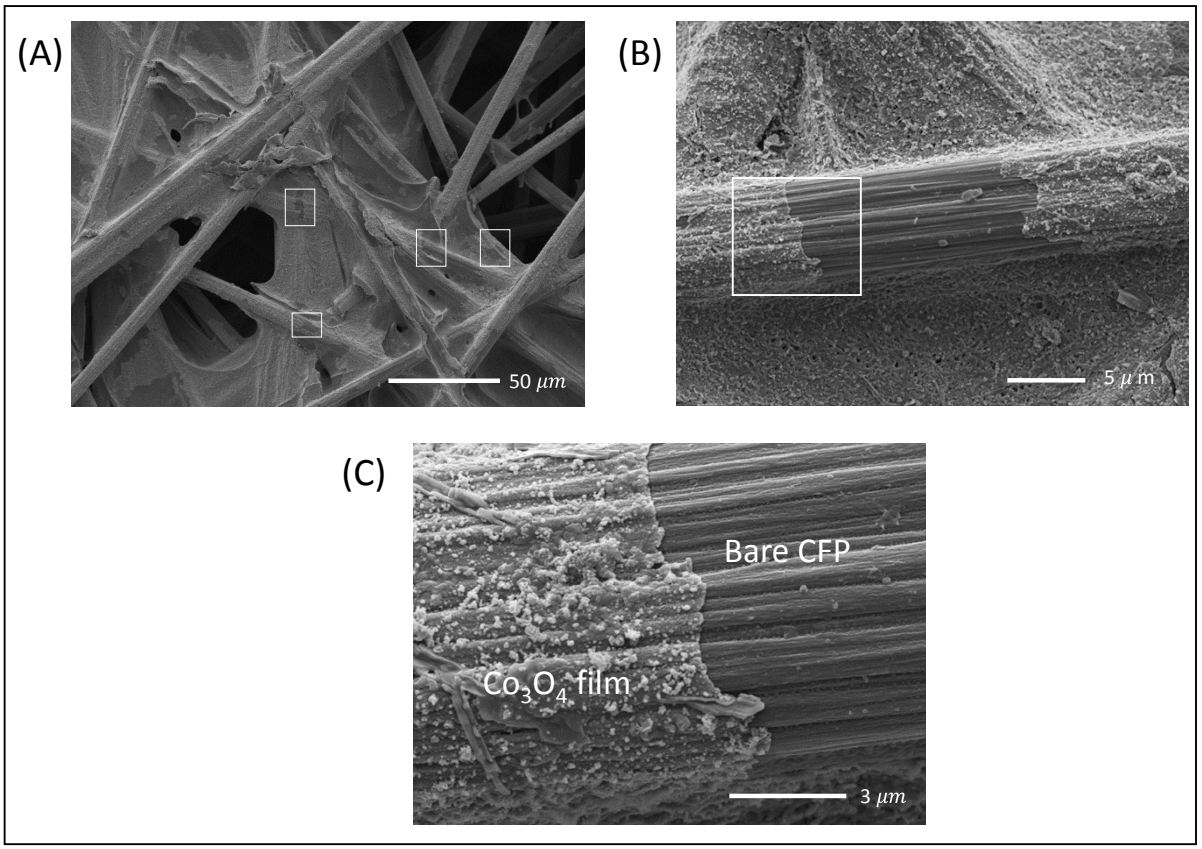

Figure S2. SEM images of Co_3O_4/CFP prepared by the topotactic method. (C) An enlarged image of the area in the white box shown in (B). The white boxes in (A) indicate the areas not covered by the Co_3O_4 thin film.

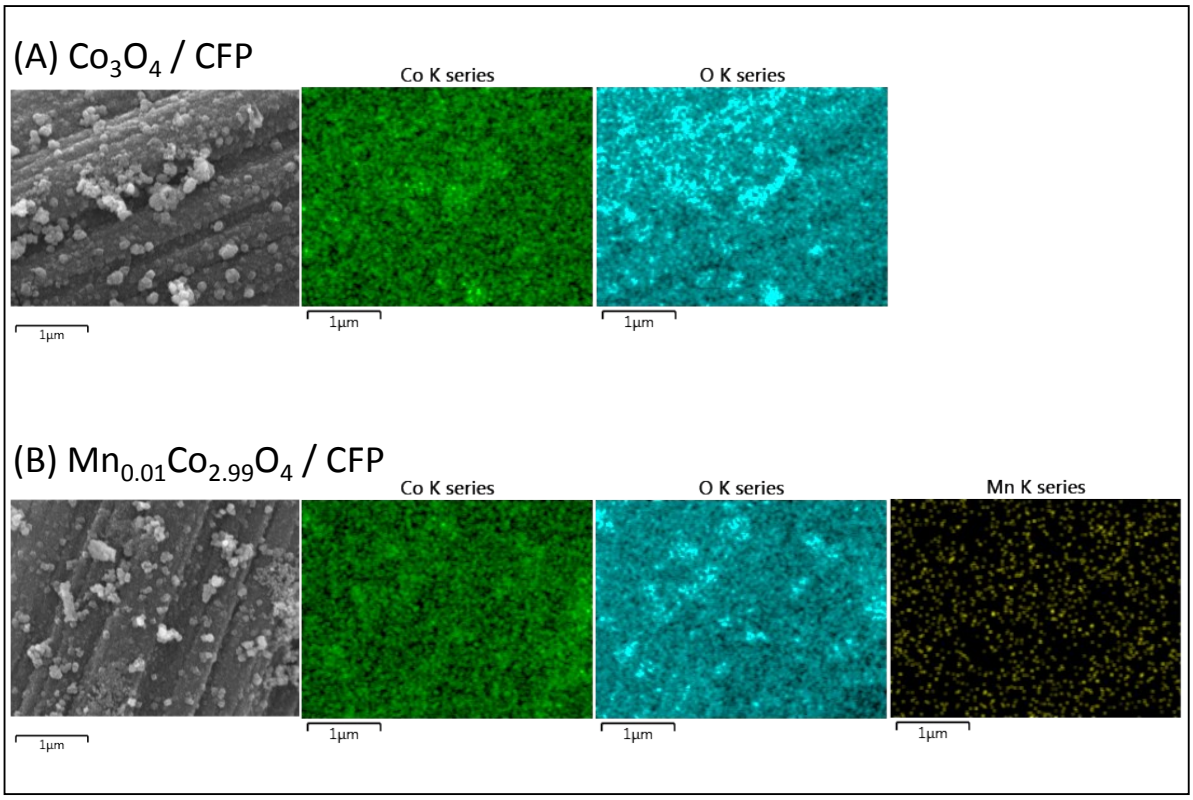

Figure S3. SEM images and elemental maps of (A) Co_3O_4/CFP and (B) $MnCo_3O_4$(0.01)/CFP films.

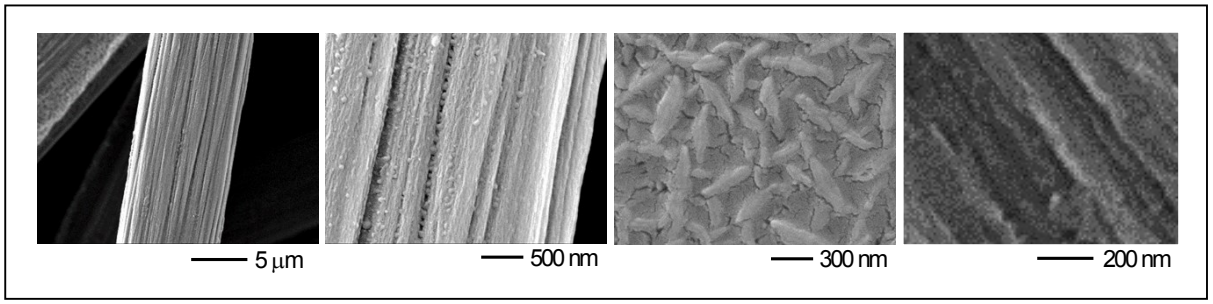

Figure S4. SEM images of bare CFP substrate.

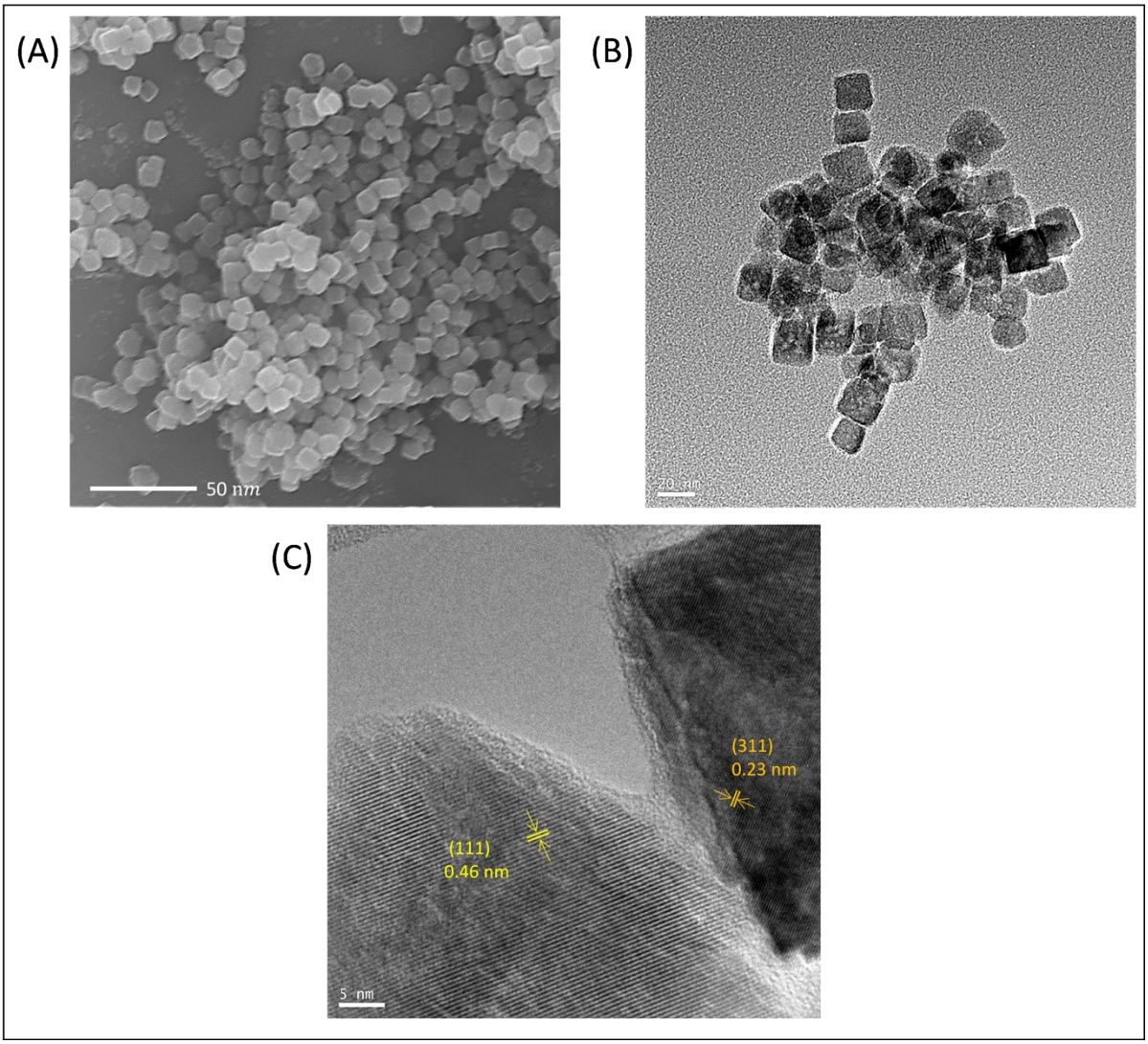

Figure S5. SEM (A), TEM (B), and HRTEM (C) images of collected nanocubes from the colloidal of the MnCoO film.

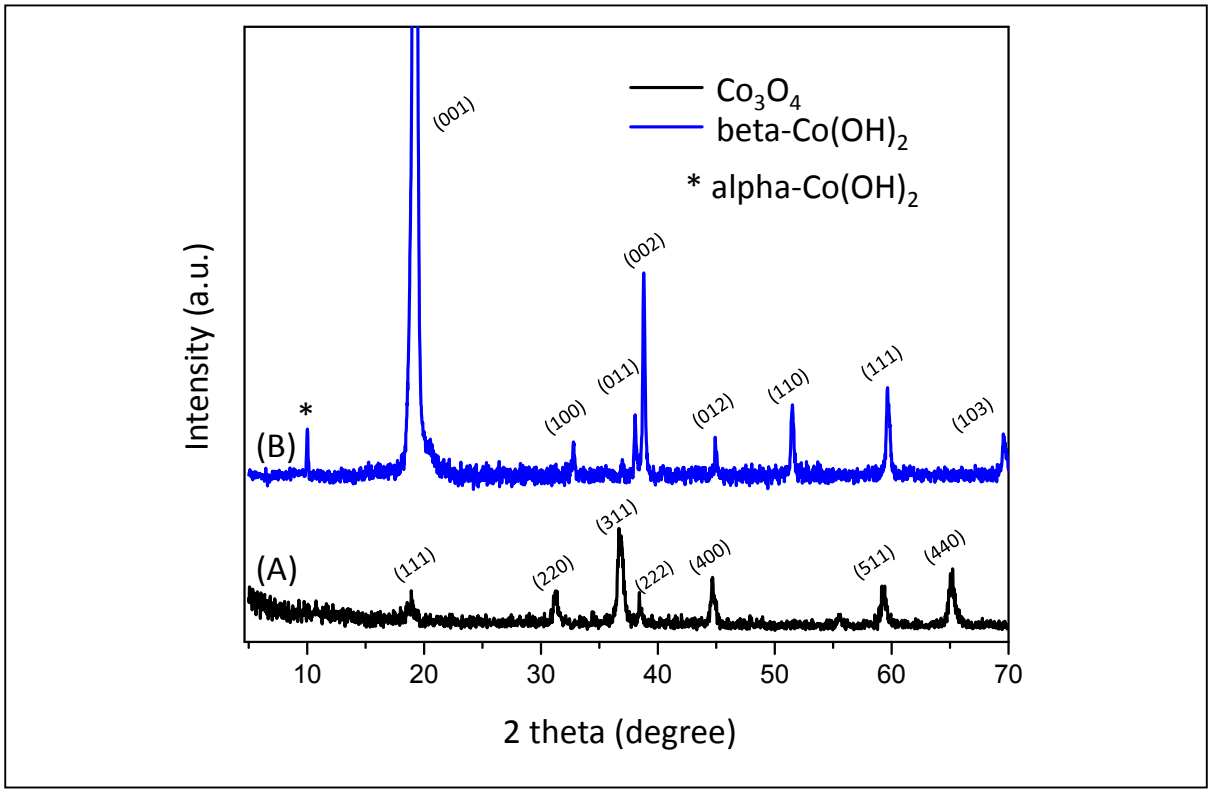

Figure S6. XRD patterns for the powdery Co_3O_4 nanoparticle samples obtained by the topotactic method and for the $Co(OH)_2$ obtained by the conventional hydrothermal method. The asterisk in (B) indicates the alpha phase of $Co(OH)_2$.

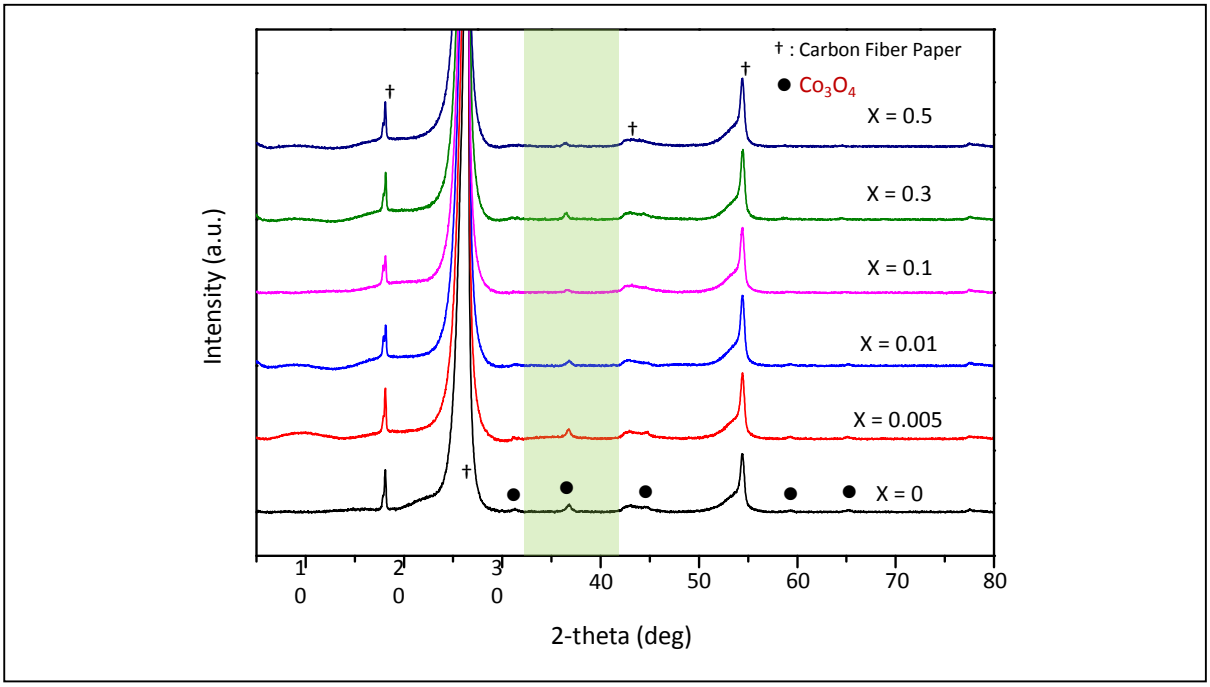

Figure S7. XRD data of $Mn_xCo_{3-x}O_4$ thin film on CFP substrate.

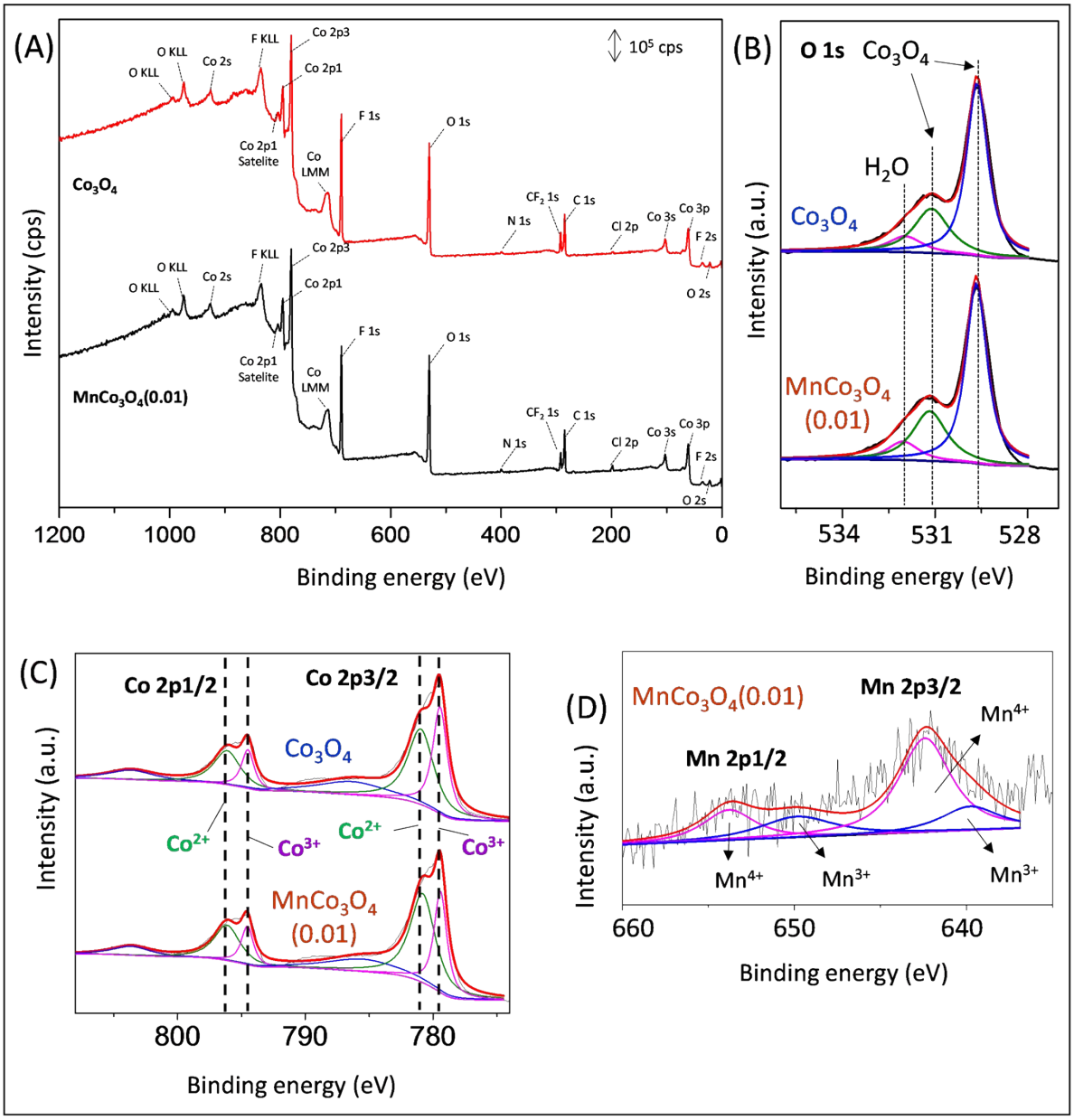

Figure S8. (A) XPS wide spectra of Co_3O_4/CFP (top) and $MnCo_3O_4$(0.01)/CFP (bottom). (B) O 1s and (C) Co 2p core-level XPS spectra of Co_3O_4/CFP and $MnCo_3O_4$(0.01)/CFP. (D) Mn 2p core-level XPS spectrum of $MnCo_3O_4$(0.01)/CFP.

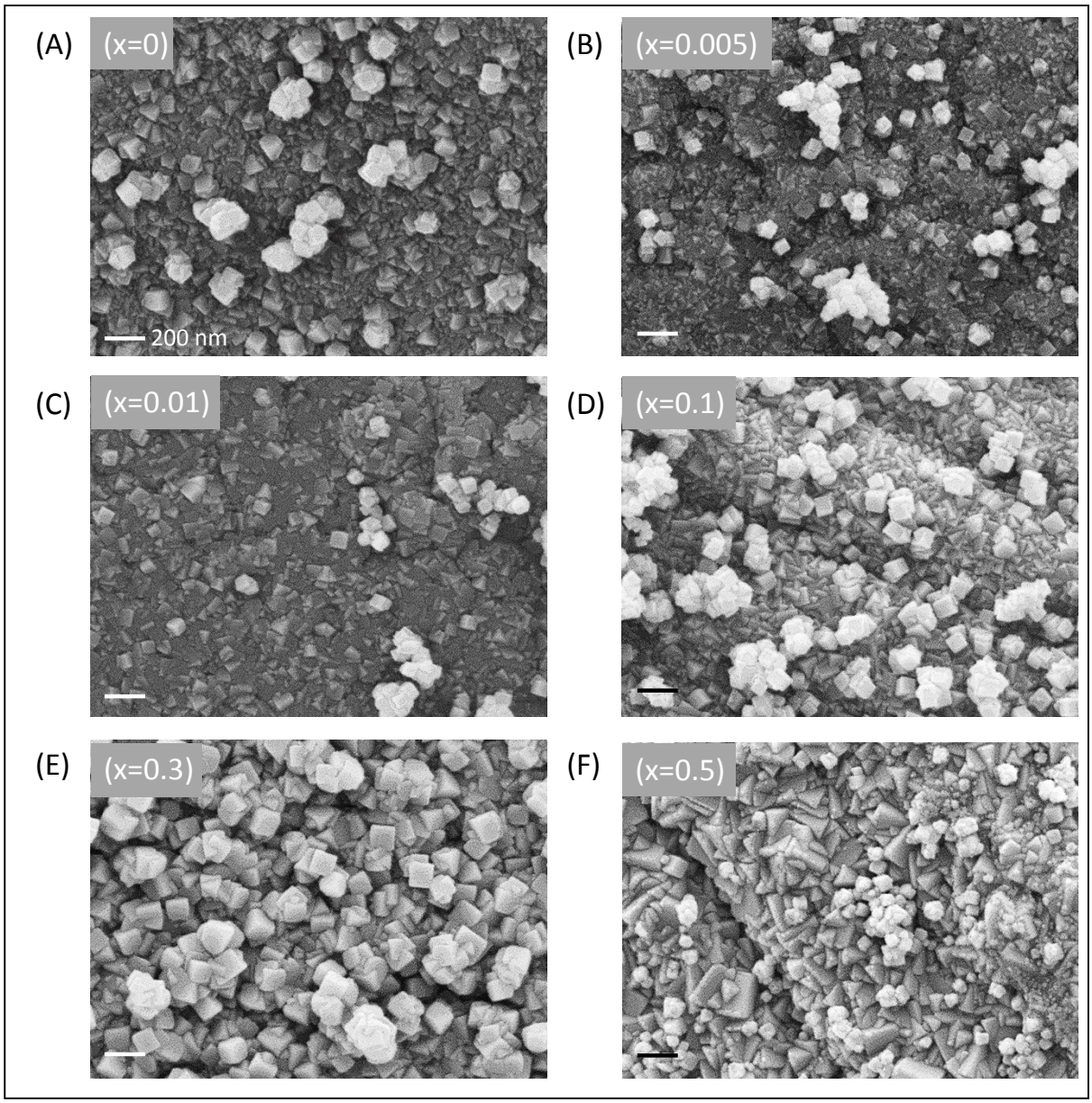

Figure S9. SEM images of the $MnxCo_3$-xO_4 thin film on CFP substrate.

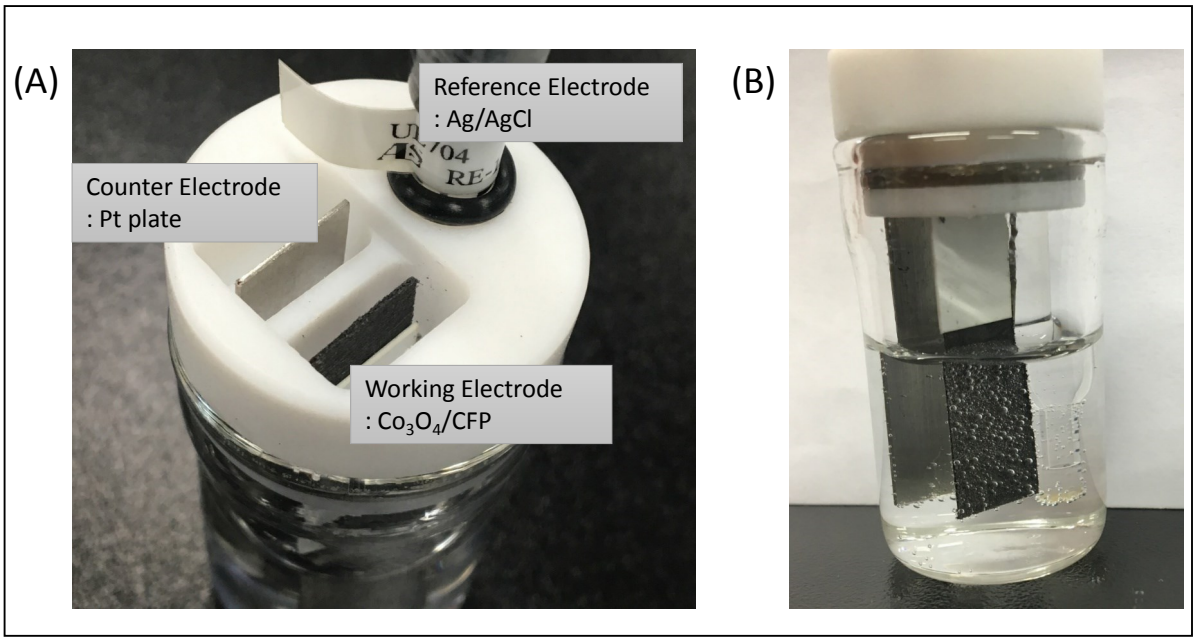

Figure S10. Top and side views of the electrode arrangement for OER measurement.

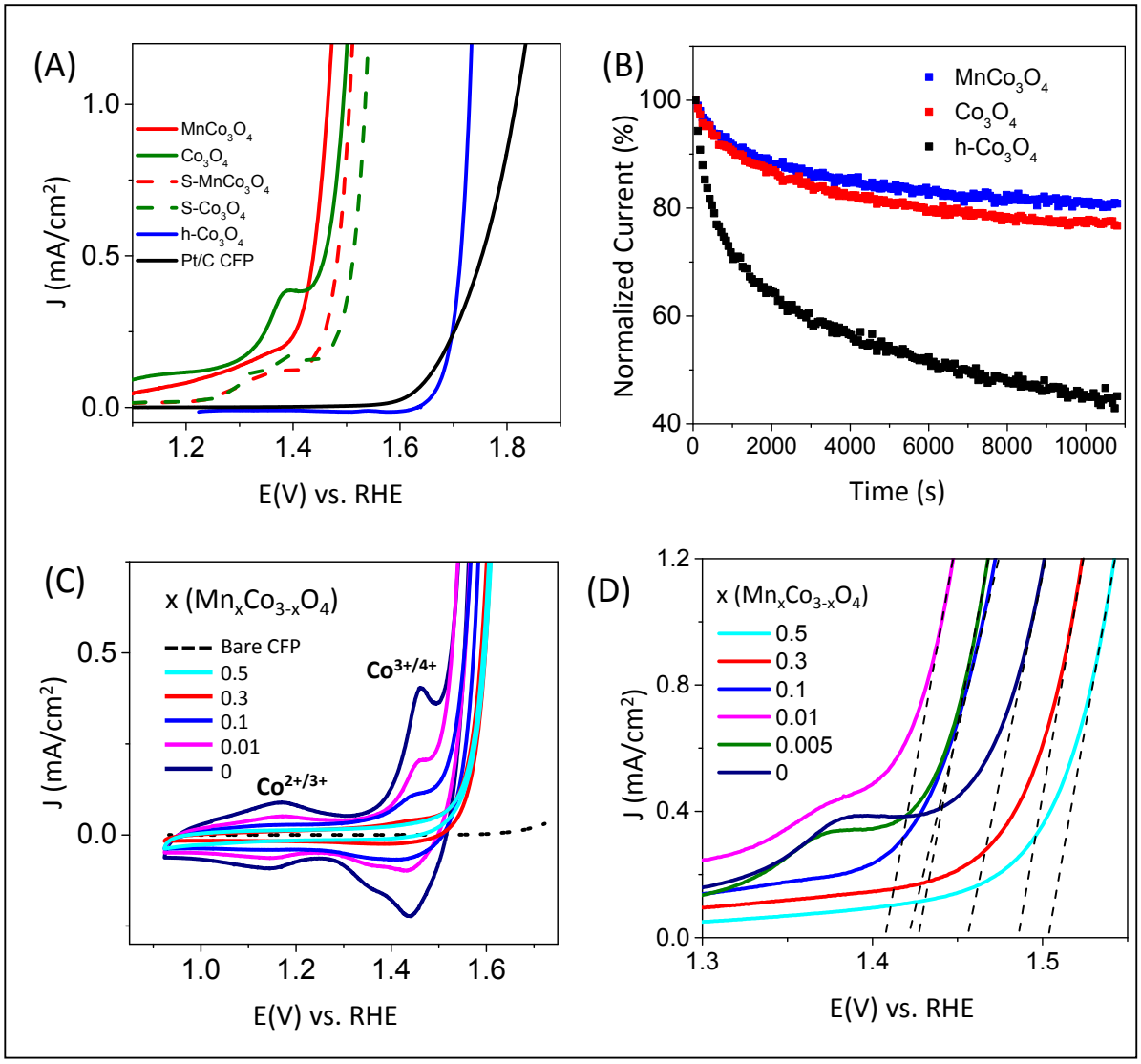

Figure S11. A) Polarisation curves and (B) chronoamperometric curves for $MnCo_3O_4$(0.01)/CFP electrode, Co_3O_4/CFP electrode, h-Co_3O_4 created via the hydrothermal method and Pt/C CFP film. (C) CV curves and (D) Polarisation curves for $Mn_xCo_{3-x}O_4$/CFP electrodes. All measurements were conducted in 1.0-M KOH at ambient temperature. In (A), S-$MnCo_3O_4$ and S-Co_3O_4 correspond to the $MnCo_3O_4$(0.01)/CFP and Co_3O_4/CFP electrode samples after undergoing durability tests for 10,000 s at a 1.85-V working potential. The normalised current densities of each sample shown in (B) were collected at a 1.85-V working potential. CVs were performed with 10 mV/s of scan rate in 1.0 M KOH.

Table S1. Summary of onset potentials and required potentials for 10 mA/cm^2. The blank values were obtained after the durability test for 10,000 s at a 1.85-V working potential.

Samples	Co_3O_4	Mn0.005	Mn0.01	Mn0.1	Mn0.3	Mn0.5	h-Co_3O_4	Pt/C
Onset potential (V)	1.46 (1.48)	1.43	1.41 (1.44)	1.43	1.49	1.50	1.65	1.62
Potential for 10 mA/cm2 (V)	1.59 (1.62)	1.56	1.54 (1.59)	1.57	1.61	1.63	1.80	2.38

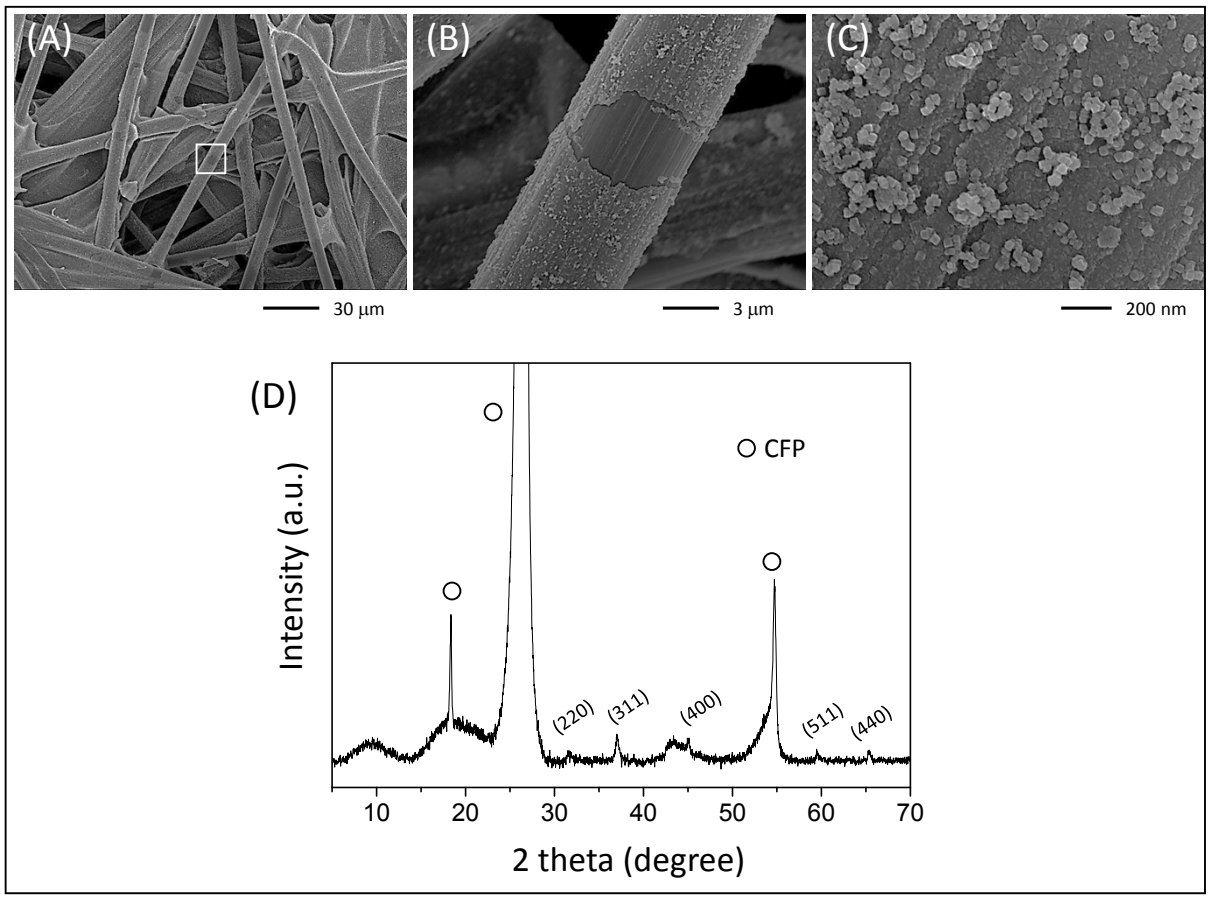

Figure S12. SEM images (A-C) and XRD pattern (D) of $MnCo_3O_4$(0.01)/CFP electrode after durability test for 10,000s. The white boxes in (A) is enlarged in (B).