## **Electronic Supplementary Information**

# Unraveling critical effects of the preoxidation process toward morphological evolution and intrinsic properties of novel ZnCoMn trimetallic hydroxides

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**Materials and chemicals:** FTO-coated glass (12 $\Omega$ /sq., 25 mm x 15 mm) was employed as the substrate for thin film electrode fabrication. Bismuth (III) nitrate pentahydrate ( $\geq$ 98%), vanadium(IV)-oxy acetylacetonate, acetic acid (99.7%), 2,4-pentanedione (99.5%), cobalt (II) sulfate hexahydrates, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (99%) were purchased from Sigma Aldrich. Zinc sulfate hexahydrates, manganese sulfate (II) monohydrate were obtained from Acros. All the chemicals were used as-obtained without any further purification. Mill-Q water (18 M  $\Omega$ .cm) was used for solutions preparation.

**Preparation of BiVO<sub>4</sub> substrates:** Spin-coated bismuth vanadate thin films were prepared using a procedure adapted from our previously reported study<sup>1</sup> with slight modification for improving stability. FTO films with nominal resistivity of ~12 Ω/cm<sup>2</sup> on 25 × 15 cm<sup>2</sup> glass substrates were thoroughly washed with pure deionized water (DI), acetone, isopropanol, dried with a nitrogen gun before deposition of BiVO<sub>4</sub> by spin coating. In a typical deposition, 0.299 g Bi(NO<sub>3</sub>)<sub>3</sub> and 0.2457 g vanadium(IV)-oxyacetylacetonate was dissolved in 18.5 mL mixture of acetylacetone and acetic acid (8.25:1, v/v). Dark green solution was sonicated for 20 min, then was filtered with 0.22 µm nylon filters (Thermo Fisher Scientific). 65µL/cm<sup>2</sup> dispensed onto the FTO/glass slide. The substrate was then spun twice in a row at 2500 r.p.m. for 20 s on a spin coater. After this spin-coating cycle, the substrate was annealed for in air at 500 °C in a muffle furnace. For the first three layers, the sample was heated for 10 min. From layer 4 to 6, after each layer deposition, sample was maintained at 500°C for 2h. After the last spin-coating cycle, the substrate was annealed for BiVO<sub>4</sub> and final thickness of ~300 nm. During the period of temperature elevation to 500°C, the heating rate was set at 3° C/min.

**Material characterizations:** Surface morphology of the films were examined by field emission scanning electron microscope (FE-SEM, JEOL JSM-6700) at an accelerating voltage of 15 kV. The crystalline structures were characterized by Bruker D2 Phaser X-ray Diffraction (XRD) in the region of  $2\theta$ =10-70° using Cu K $\alpha$  radiation ( $\lambda$ =0.15418 nm). Optical properties were studied by doubled-beam UV-Vis spectrophotometer (Jasco V670, Japan) attached with an integrating sphere. Raman spectra were recorded with a *NRS-5100* series spectrometer (Jasco, Japan) using a 532 nm laser with a 50 mV power source and an optical density of 6 (OD 6). X-ray photoelectron spectroscopy (XPS, VGS Thermo Scientific) with Al K $\alpha$  X-ray radiation as the X-ray source was used for surface chemical analyses.

The mass concentration and molar ratio of ZnCoMn LDH were studied with an inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Jobin Yvon JY-2000). Samples for ICP-AES were prepared by dissolving ZnCoMn films ( $2 \text{ cm} \times 2 \text{ cm}$ ) in concentrated nitric acid, followed by the dilution with DI water to 10 mL in volume.

Hall measurements for the electrical resistivity, carrier concentration, and mobility of the ZnCoMn-LDH nanocomposites was measured with four-point probe method (Ecopia, HMS-3000, Korea) in a constant magnetic field of 0.55 T at room temperature.

Surface hydrophilicity of LDH films were determined by using an apparatus of video-imageenhanced sessile drop tensiometer. The apparatus was composed of a drop formation system includes a stainless-steel needle (#28 and ID = 0.18 mm), an image system containing a light source (Oriel, QTH 63200) and a solid-state video camera (MS-4030 charge-coupled device, Sierra, Scientific Co.), was used for sequentially recording the water drops on solid substrates. The frequency of frame taken was 30 images per second. The initial water drop diameter was controlled and the water drop was gently deposited on the substrate. **Electrochemical studies:** The photoelectrochemical experiments were carried out under simulated AM 1.5G illumination (100 mWcm<sup>-2</sup>) provided by a solar simulator (500W Xenon lamp, Model 66905, Newport). 0.1M sodium borate aqueous solution was used as an electrolyte. A three-electrode configuration was used in the measurement, with the LDHs on BiVO<sub>4</sub> substrate serving as the working electrode (photoanode), an Ag/AgCl (3M KCl) as the reference electrode, and a platinum mesh (2.5cm x 2.5cm) as the counter electrode. Photocurrent *vs.* voltage (I–V) characteristics were recorded by scanning the potential from -0.6 to 0.6 V (*vs.* Ag/AgCl (3 M KCl)) with a scan rate of 20 mV s<sup>-1</sup> using an electrochemical analyzer potentiostat (Autolab PGSTAT302N, Switzerland). The measured potentials vs Ag/AgCl (3 M KCl) were converted to the reversible hydrogen electrode (RHE) scale using the relationship  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059$  pH  $+ E^0_{\text{Ag/AgCl}}$ , where  $E_{\text{Ag/AgCl}}$  is the experimentally measured potential, and  $E^0_{\text{Ag/AgCl}} = 0.21$  V at 25 °C for an Ag/AgCl electrode in 3 M KCl.

H <sub>2</sub> O <sub>2</sub> concentration (mM)	Zn (%at.)	Co (%at.)	Mn (%at.)	Conductivity (1/Ωcm)	Carrier concentration (cm <sup>-3</sup> )
No H <sub>2</sub> O <sub>2</sub>	78.6	12.3	9.1	6.87E+02	2.22E+20
32	67.9	14.1	17.9	1.34E+03	2.98E+20
80	55.8	12.9	31.3	1.50E+03	5.09E+20
120	55.1	12.2	32.7	1.23E+03	3.05E+20

Table S1 Evolution of molar percentage of metal ions (Zn, Co, and Mn) in ZnCoMn-LDH/BiVO<sub>4</sub> as a function of different hydrogen peroxide concentration.

Table S2 ICP-AES data of ZnCoMn-LDH as a function of hydrogen peroxide concentration

H <sub>2</sub> O <sub>2</sub> concentration (mM)	Zn (ppm)	Co (ppm)	Mn (ppm)	Atomic ratio (Zn : Co : Mn)
No H <sub>2</sub> O <sub>2</sub>	0.38	0.14	0.1	61.3 : 22.6 : 13.9
32	1.36	0.25	0.25	73.2 : 13.4 : 13.4
80	3.31	1.06	2.04	51.6 : 16.5 : 31.8
120	2.59	0.7	1.51	53.9 : 14.5 : 31.5

### Table S3 Solubility product constant <sup>2</sup>

Compound	Ksp
Zn(OH) <sub>2</sub>	3*10-17
Co(OH) <sub>2</sub>	5.9*10 <sup>-15</sup>
Mn(OH) <sub>2</sub>	1.9*10-13
Co(OH) <sub>3</sub>	1.6*10 <sup>-34</sup>
Mn(OH) <sub>3</sub>	<b>2*10</b> -36



Figure S1 Cross-section TEM profile scanning area, with indications of scanned points and

#### corresponding EDS results

Table S4 The respective concentrations for Zn, Co, Mn at point A, B and C obtained from TEM-EDS point scan

Point	Zn (%at.)	Co (%at.)	Mn (at. %)
А	43.2	17.4	39.4
В	38.3	25.1	36.6
С	0	6.9	93.1

The relative electrochemical active surface area of each catalyst as a function of hydrogen peroxide addition was measured from their electrochemical capacitances ( $C_{dl}$ ) using a simple cyclic voltammetry method. The double layer current is equal to the product of the scan rate and the capacitance, which is expected to be linearly proportional to the active surface area of electrode. By plotting the capacitive currents versus scan rate, the capacitance can be estimated as the slope.

As shown in **Fig. S2**, ZnCoMn-LDH obtained from the electrodeposition with 80 mM hydrogen peroxide has a much larger  $C_{dl}$  of 17.1 mF cm<sup>-2</sup> than other electrodes, which could be attributed to its uniform formation of 2D nanosheet.



Fig. S2 Electrochemical capacitance measurements of the relative ECSA of ZnCoMn-LDH with different added H<sub>2</sub>O amount (a) without H<sub>2</sub>O<sub>2</sub>, (b) 32 mM, (c) 80 mM and (d) 120 mM



Fig. S3 XRD pattern of ZnCoMn-LDH powder scratched from BVO substrate and reference patterns of hydrotalcite (LDH)



Figure S4 Properties of water drop on the surface of ZnCoMn-LDH with different added H<sub>2</sub>O<sub>2</sub>



Fig. S5 Chronoamperometry curve of optimized ZnCoMn-modifed BiVO<sub>4</sub> at 1.23 V in NaBi (pH 9.3)

OER catalyst	Photocurrent density (mA/cm <sup>2</sup> )	Electrolyte	Ref.
NiFe-LDH/BiVO <sub>4</sub> /Fe <sub>2</sub> O <sub>3</sub>	~0.9	1 M NaOH	3
ZnCo-LDH/Fe <sub>2</sub> O <sub>3</sub>	1.14	1M KOH	4
ZnFe-LDH/TiO <sub>2</sub>	1.26	0.5 M Na <sub>2</sub> SO <sub>4</sub>	5
CoFe-LDH/TiO <sub>2</sub>	0.68	1M KOH	6
CoCr-LDH/TiO <sub>2</sub>	0.76	1M KOH	7
NiFe-LDH/Graphene/TiO <sub>2</sub>	1.18	0.5 M Na <sub>2</sub> SO <sub>4</sub>	8
NiFe-LDH/WO <sub>3</sub>	0.8	0.2 M Na <sub>2</sub> SO <sub>4</sub>	9

**Table S5** Top-performance LDH-decorated photoanodes (measured at a standard illumination of AM1.5 G, obtained at 1.2–1.23 V vs. RHE).

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