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Supplementary Information

Continuously Oxygen Vacancy Engineering of Co_3O_4 Layer for Enhanced Alkaline Electrocatalytic Hydrogen Evolution Reaction

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Part I: Experimental Section

1.1 Synthesis of the O_v-engineered Co_3O_4 layer

Before use, nickel foams (0.5 cm × 0.6 cm × 0.3 mm) were soaked in 3 M HCl for 20 min to remove impurities on the surface. The O_v-engineered Co_3O_4 layer was synthesized by a rapid solid-phase melting strategy. In a typical synthesis of the medium crystallinity Co_3O_4 layer (M-Co_3O_4), 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$ were put into a 3 mL flask. Then, a piece of Ni foam was inserted into the flask and heated to 200 ^{o}C for 20 min in a muffle furnace in static air. After cooled down to room temperature, washed with distilled water and absolute ethanol for three times, the M-Co_3O_4 sample was obtained. The crystallinity of Co_3O_4 film can be regulated by changing reaction temperature to 160 and 240 ^{o}C in the synthesis of Co_3O_4 layers with high and low O_v contents (H-Co_3O_4 and L-Co_3O_4), respectively.

1.2 Characterization

The X-ray powder diffraction (XRD) patterns were measured on a Rigaku D/Max 2550 diffractometer with Cu Kα radiation at a scan rate of 1° min^{-1}. The hydrophilic-hydrophobic properties were measured by Harke, SPCA-X-3 meter. The scanning electron microscope (SEM) and transmission electron microscope (TEM) images were obtained from Hitachi, S-4800 at an accelerating voltage of 15.0 kV and Tecnai, G2F30 S-Twin with an energy-dispersive X-ray spectrometer (EDX) at an accelerating voltage of 200.0 kV, respectively. Inductively coupled plasma mass spectrometry (ICP-MS) was recorded by an Agilent 7700 spectrometer. The electrical conductivities were measured using a model RTS-8 four-point probe meter.X-ray photoelectron spectroscopy (XPS) spectra were recorded by an

ESCALAB 250Xi X-ray photoelectron spectrometer at a pass energy of 40 eV with an Al Kα X-ray source.

1.3 Electrochemical Measurements

All electrochemical measurements applied in a CHI660E electrochemical workstation (Chenhua, Shanghai) were carried out in a standard three-electrode system consisting of a saturated Ag/AgCl reference electrode, a graphite counter electrode and a 30 mL 1.0 M KOH electrolyte. The samples grown on nickel foam were directly applied as working electrode. The measured potential was calibrated to reversible hydrogen electrode (RHE) potential according to the following equation:

$$E_{RHE} = E_{Ag/AgCl}+0.1976+0.0591\times pH$$

Prior to HER measurement, pure N_2 was purged into electrolyte to reach N_2-saturated condition. The N_2 flow remained during the whole test process. HER polarization curves were recorded by linear sweep voltammetry technique at a scan rate of 1 mV s^{-1}. The stability of electrocatalysts was measured by chronopotentiometry at constant current densities of 10, 50 and 100 mA cm^{-2}, respectively. Electrochemical impedance spectroscopy (EIS) was performed at -0.2 V *vs.* RHE in a wide frequency ranging (10 kHz - 100 mHz) with a current voltage amplitude of 5 mV. Ohmic resistance was estimated from the EIS results at a phase angle of 0° in high frequency. All data was compensated with 95% iR correction. Electrochemically active surface area (ECSA) was calculated by the following equation:

$$ECSA=C_{DL}/C_S$$

where C_{DL} is double layer capacitance, C_S is specific capacitance. The C_{DL} is obtained through the multi-rate CV method in non-faradic potential range,[S1] where the scan rates are 50, 100, 200, 400, 600 and 800 mV s^{-1}, respectively. The Cs of Co is 27 uF cm^{-2} in alkaline media reported by the previous literature.[S2] Turnover frequency (TOF) was estimated from the following equation:

$$TOF=J\times A/2\times n\times F$$

where J is the current density in HER polarization curves, A is geometric area of electrode, F is Faraday constant (C mol^{-1}), and n is mole number of active sites on the electrode.

Part II: Supporting Figures

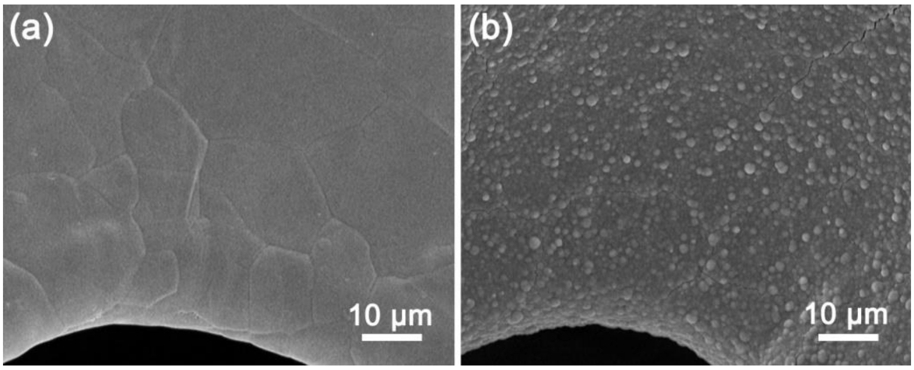

Fig. S1 Low-magnification SEM images of the (a) pristine Ni foam and (b) M-Co_3O_4.

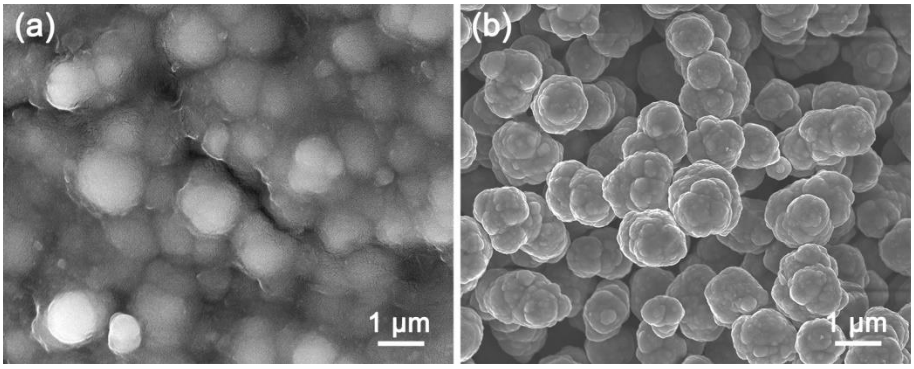

Fig. S2 SEM images of the (a) H-Co_3O_4 and (b) L-Co_3O_4 samples.

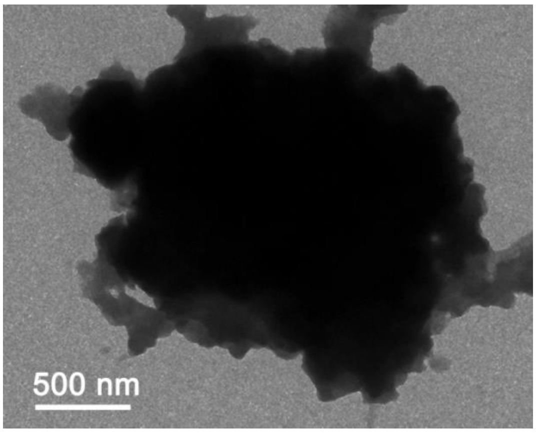

Fig. S3 Low-magnification TEM image of the M-Co_3O_4 sample.

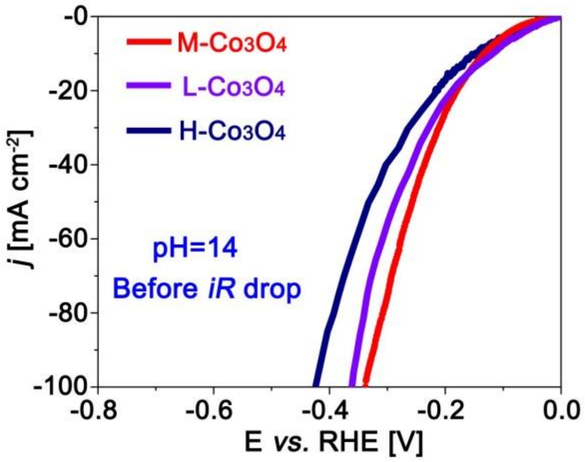

Fig. S4 HER polarization curves of the Co_3O_4 samples before iR drop.

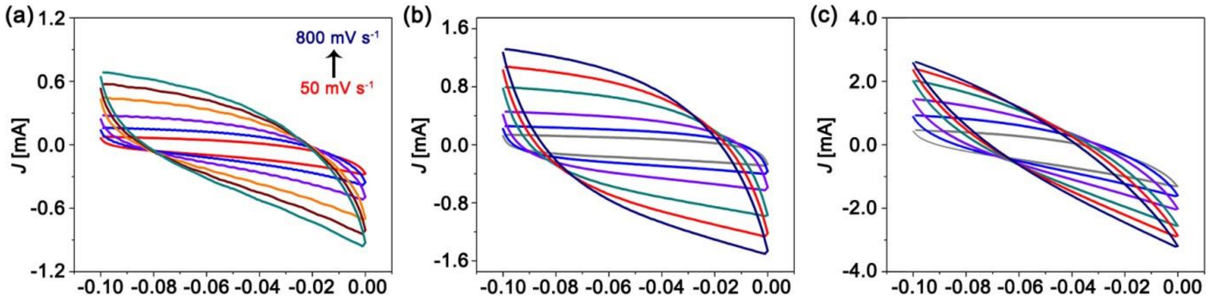

Fig. S5 Cyclic voltammogram curves of the H-Co_3O_4, M-Co_3O_4 and L-Co_3O_4 electrodes in the non-faradic potential range at different sweep rates.

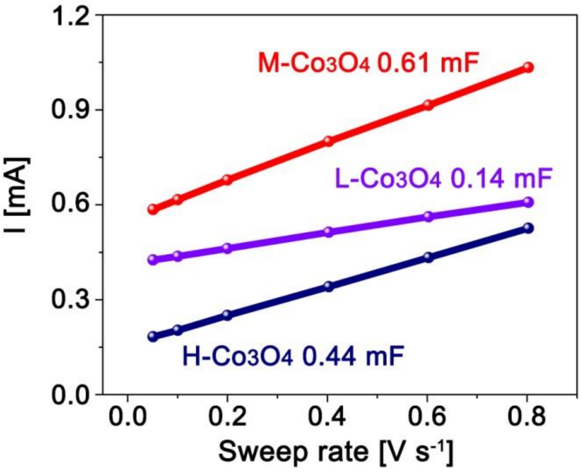

Fig. S6 Capacitive currents as a function of sweep rate of the H-Co_3O_4, M-Co_3O_4 and L-Co_3O_4 electrodes measured at 0.96 V *vs.* RHE. The double-layer capacitances are calculated from the slope of the linear fitting to the data.

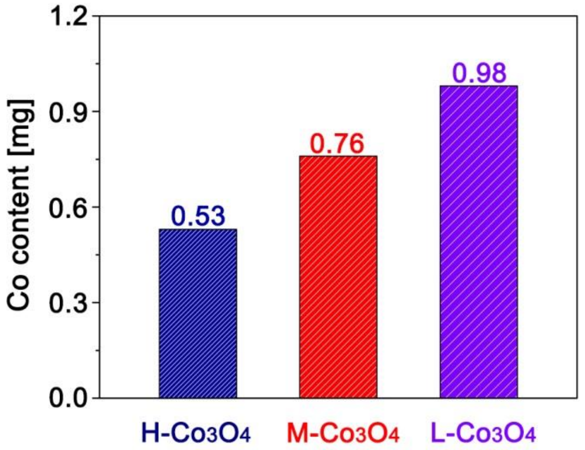

Fig. S7 Co contents of the H-Co_3O_4, M-Co_3O_4 and L-Co_3O_4 samples on Ni foam.

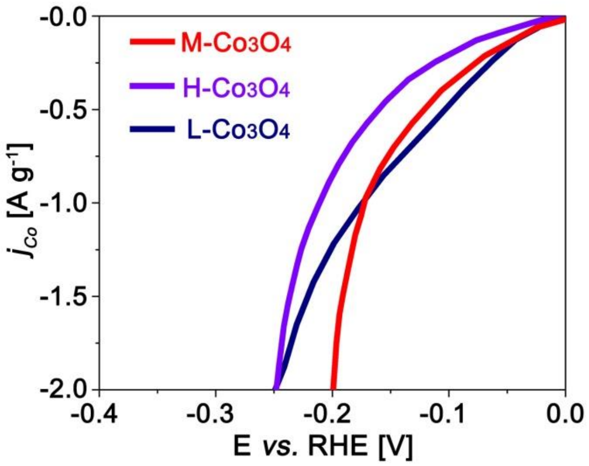

Fig. S8 Mass-normalized HER polarization curves of the H-Co_3O_4, M-Co_3O_4 and L-Co_3O_4 electrodes.

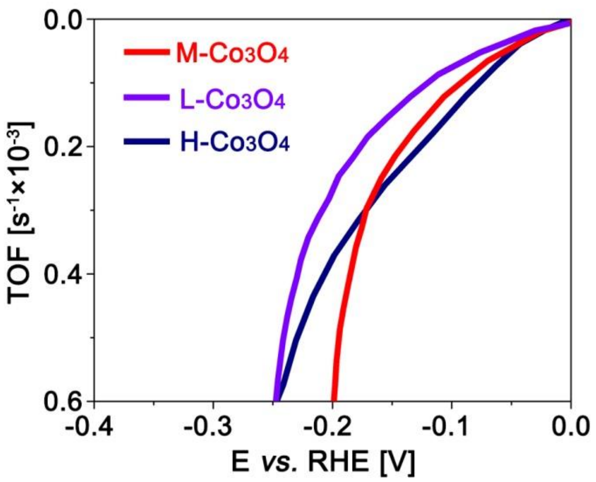

Fig. S9 Turnover frequencies of the H-Co_3O_4, M-Co_3O_4 and L-Co_3O_4 electrodes.

Part III: Supporting Table

Table S1 Comparison of HER performances of the reported Co_3O_4 electrocatalysts.

Catalyst	**Measurement**	**Loading (mg cm^{-2})**	**J (mA cm^{-2})**	**η (mV)**	**Tafel slope (mV dec^{-1})**	**Ref.**
Phosphorus-doped Co_3O_4 nanowire array	Ni foam 1.0 M KOH	10.7	-10 -100	97 205	86	10
Co-P@Co_3O_4	Carbon cloth 1.0 M KOH	3.0	-10	73	85	11
Octahedral Co_3O_4 particles	Co foam 1.0 M KOH	3.9	-10 -100	78 210	88	12
Co_3O_4 nanocrystals	Carbon fiber 1.0 M KOH	0.35	-10	380	116	13
Co\Co_3O_4 nanosheets	Ni foam 1.0 M KOH	0.85	-10 -100	90 240	44	14
Co_3O_4 nanorods	Co foil 1.0 M KOH	2.2	-10	268	\	15
Urchin-like Co_3O_4 sphere arrays	Ni foam 1.0 M KOH	4.2	-10	225	68	16
Hollow Co_3O_4 microtube arrays	Ni foam 1.0 M KOH	\	-100	292	98	17
M-Co_3O_4	**Ni foam 1.0 M KOH**	**1.03**	**-10 -50 -100**	**71 180 203**	**63**	**This work**
L-Co_3O_4	Ni foam 1.0 M KOH	1.33	-10 -50 -100	79 209 249	107	This work
H-Co_3O_4	Ni foam 1.0 M KOH	0.72	-10 -50 -100	82 243 301	143	This work

References

[S1] C. C. L. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2013, **135**, 16977-16987.

[S2] G. Wu, N. Li, D. R. Zhou, K. Mitsuo and B. Q. Xu, *J. Solid State Chem.*, 2004, **177**, 3682-3692.