Supporting Information

Clarifying the controversial catalytic active sites of Co_3O_4 for oxygen evolution reaction

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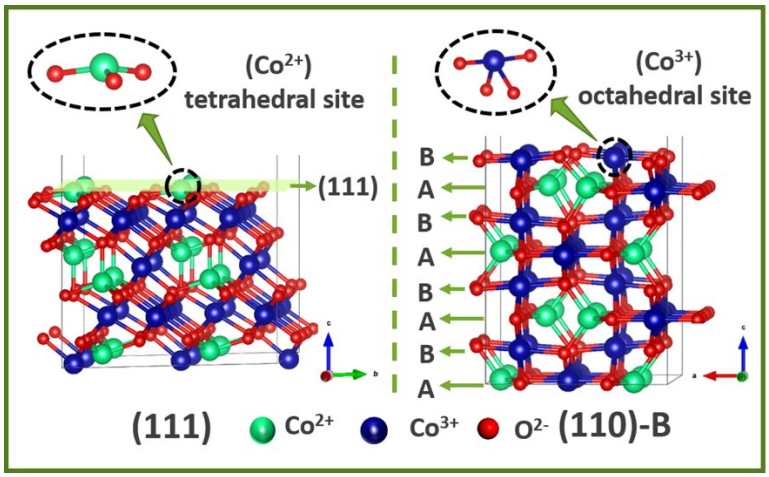

Fig. S1 The side-view of Co_3O_4 structure and the surface atomic configurations in the (111) plane (right) and the (110)-B plane (left).

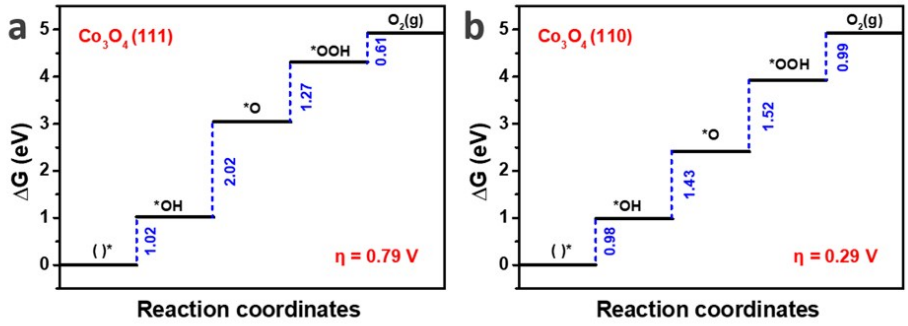

Fig. S2 The calculated OER free energy diagram over the (111) plane (a) and (110)-B plane (b) of Co_3O_4. Free energy diagram for Co_3O_4 (111) and Co_3O_4 (110)-B for OER at zero potential (U = 0).

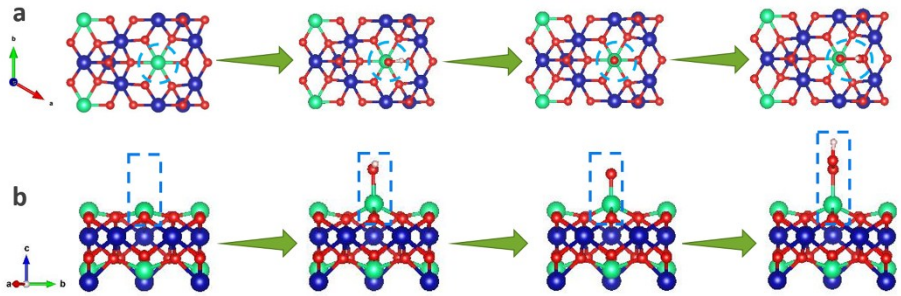

Fig. S3 Adsorption configurations over the (111) plane of Co_3O_4, (a) top-view and (b) side-view.

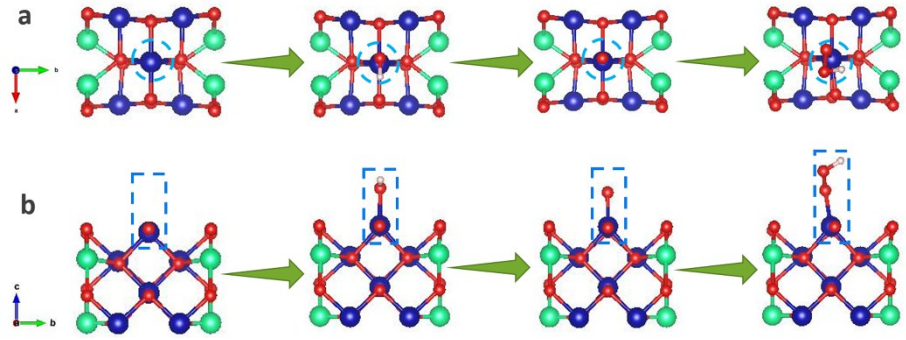

Fig. S4 Adsorption configurations over the (110)-B plane of Co_3O_4, (a) top-view and (b) side-view.

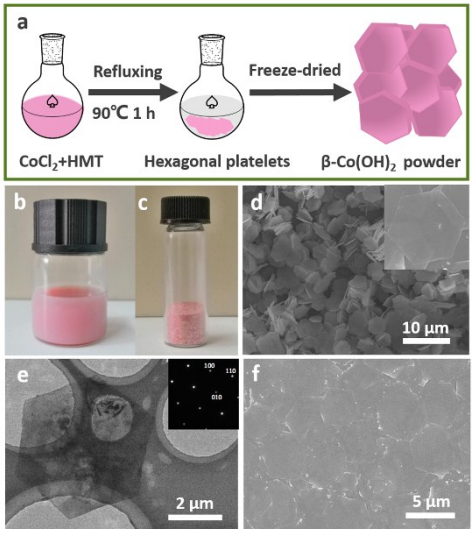

Fig. S5 (a) Schematic illustration of the synthesis for hexagonal platelets of β-$Co(OH)_2$-5.0. (b) The suspension of β-$Co(OH)_2$-5.0 in ethanol. (c) The powder of the β-$Co(OH)_2$-5.0 hexagonal platelets made by freeze-dried. (d) SEM images of β-$Co(OH)_2$-5.0 hexagonal platelets at low and high magnification (Inset). (e) TEM image of β-$Co(OH)_2$-5.0 hexagonal platelet and typical electron diffraction pattern (Inset). (f) SEM image of β-$Co(OH)_2$-5.0 film fabricated by the hexane/water interfacial self-assembly strategy.

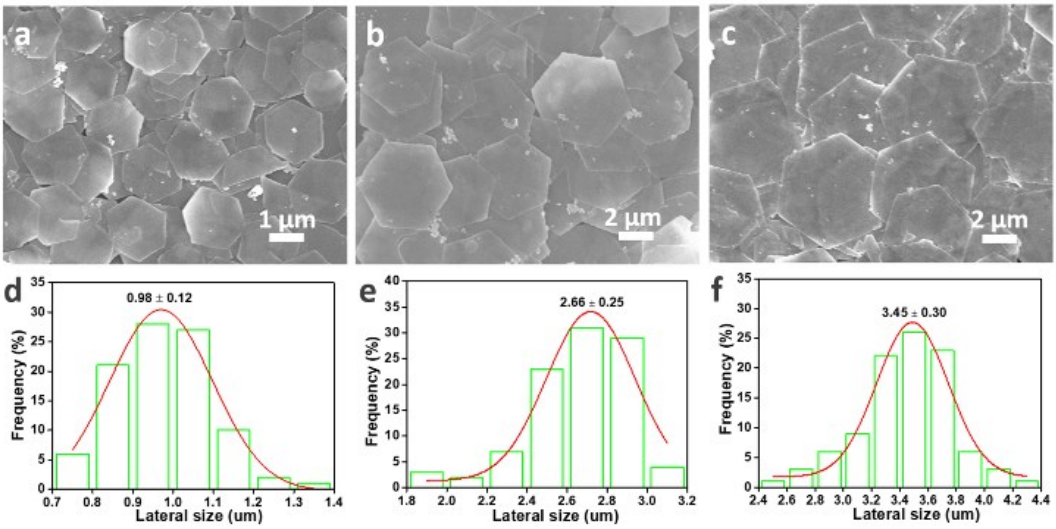

Fig. S6 (a-c) The SEM images of β-$Co(OH)_2$-2.5, β-$Co(OH)_2$-5.0 and β-$Co(OH)_2$-7.5, respectively. (d-f) The corresponding lateral size distributions of β-$Co(OH)_2$-2.5, β-$Co(OH)_2$-5.0 and β-$Co(OH)_2$-7.5.

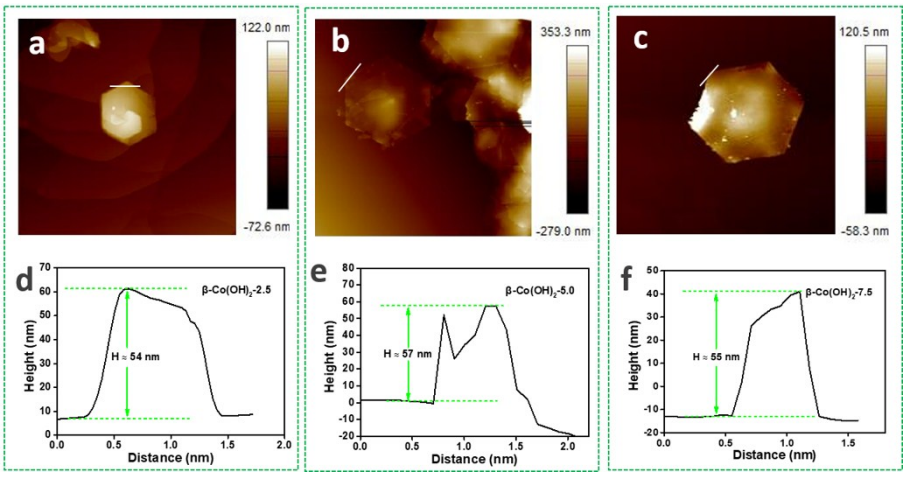

Fig. S7 AFM images of (a) β-$Co(OH)_2$-2.5, (b) β-$Co(OH)_2$-5.0 and (c) β-$Co(OH)_2$-7.5. The corresponding thickness measurement data of (d) β-$Co(OH)_2$-2.5, (e) β-$Co(OH)_2$-5.0 and (f) β-$Co(OH)_2$-7.5.

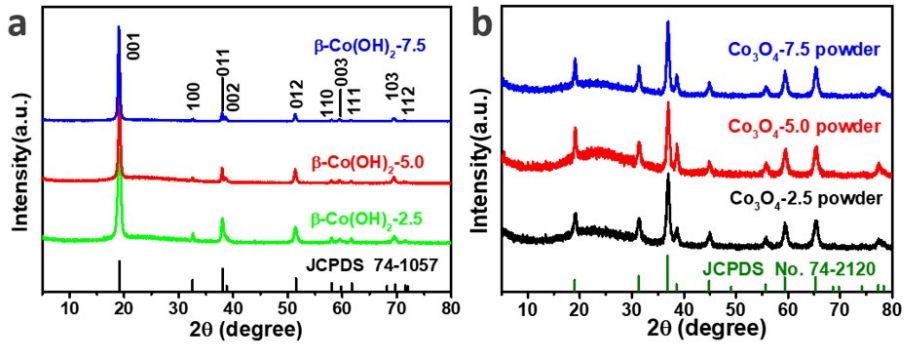

Fig. S8 (a) XRD pattern of synthesized pink powder of β-$Co(OH)_2$-2.5, β-$Co(OH)_2$-5.0 and β-$Co(OH)_2$-7.5. (b) XRD patterns of Co_3O_4-2.5, Co_3O_4-5.0 and Co_3O_4-7.5.

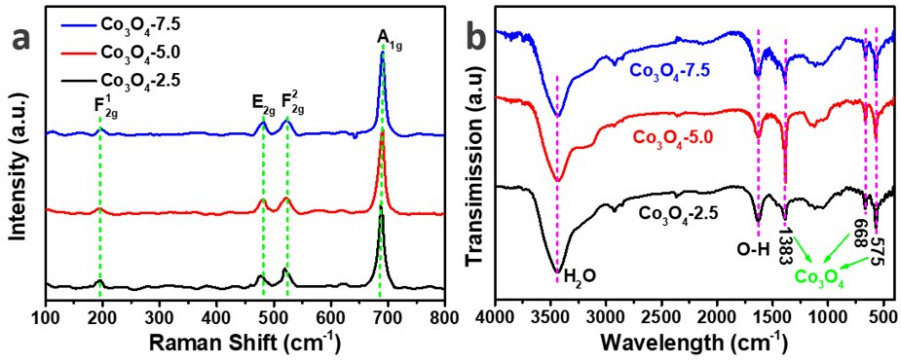

Fig. S9 (a) Raman spectra of synthesized Co_3O_4-2.5, Co_3O_4-5.0, and Co_3O_4-7.5 powder. (b) FTIR spectra of synthesized Co_3O_4-2.5, Co_3O_4-5.0, and Co_3O_4-7.5 powder.

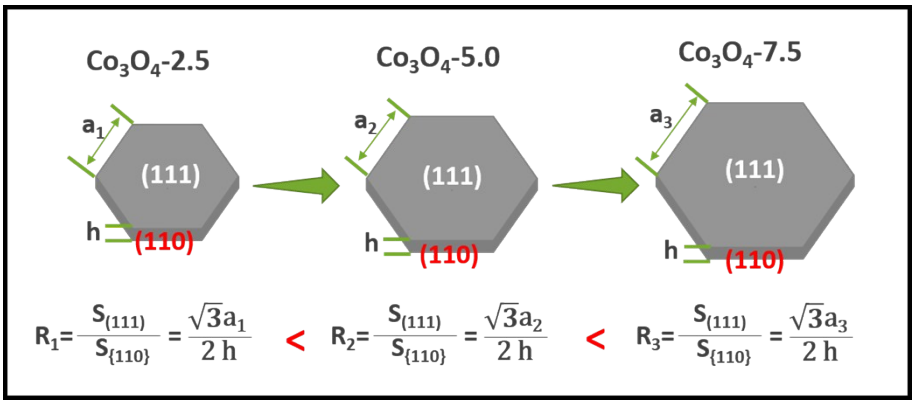

Fig. S10 Structure models of Co_3O_4-2.5, Co_3O_4-5.0 and Co_3O_4-7.5 hexagonal platelets and the corresponding ratios (**R_1**-**R_3**) of the (111) planes and {110} planes.
(**$S_{(111)}$**: the area of both top and bottom regular hexagons ((111) planes); **$S_{\{111\}}$**: the area of six side rectangles ({110} planes). **a_1**-**a_3**: the lateral sizes of Co_3O_4-2.5, Co_3O_4-5.0 and Co_3O_4-7.5, respectively. **h**: the thickness of the Co_3O_4-2.5, Co_3O_4-5.0 and Co_3O_4-7.5. **R_1** : **R_2** : **R_3** = **a_1** : **a_2** : **a_3** = 1.0 : 2.7 : 3.5.)

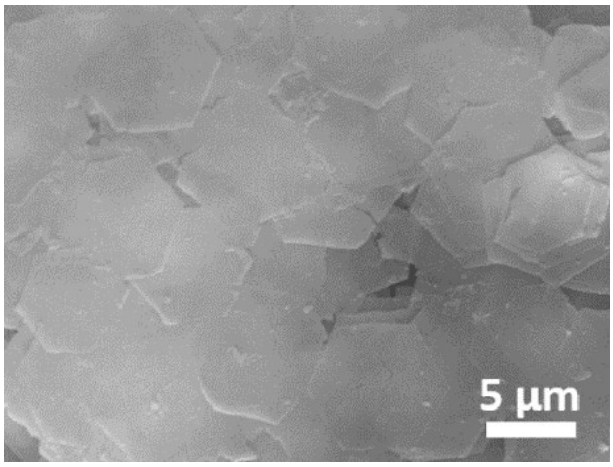

Fig. S11 The SEM images of Co_3O_4-5.0 hexagonal platelets on the surface of conductive silicon substrate.

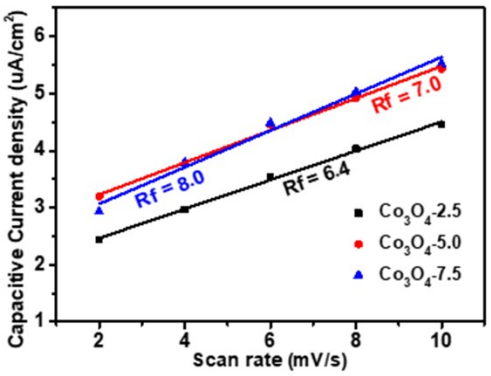

Fig. S12 Dependence relation of the capacitive current vs. scan rate for Co_3O_4-2.5, Co_3O_4-5.0 and Co_3O_4-7.5.

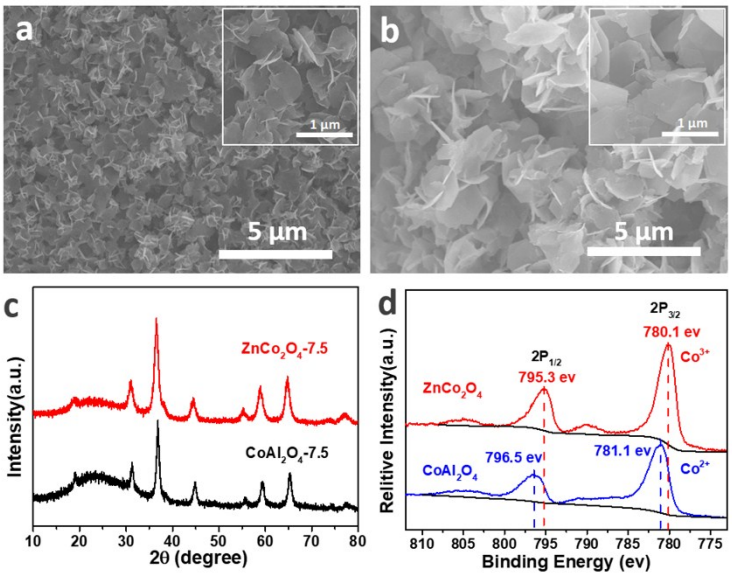

Fig. S13 (a, b) SEM images of $CoAl_2O_4$-7.5 and $ZnCo_2O_4$-7.5 at low and high (inset) magnification, respectively. (c) XRD pattern of $CoAl_2O_4$-7.5 and $ZnCo_2O_4$-7.5. (d) XPS spectra of the Co 2p in $CoAl_2O_4$-7.5 and $ZnCo_2O_4$-7.5.

(The $CoAl_2O_4$-7.5 and $ZnCo_2O_4$-7.5 were synthesised with the same method as Co_3O_4-7.5. In synthesis procedure of the precursor, the amounts of $CoCl_2 \cdot 6H_2O$ with $AlCl_3$ (Co/Al = 1/2) and $CoCl_2 \cdot 6H_2O$ with $ZnCl_2$ (Co/Zn = 2/1) were dissolved to give the total concentrations of 7.5 mM, respectively. The samples were denoted as $CoAl_2O_4$-7.5 and $ZnCo_2O_4$-7.5, respectively.)

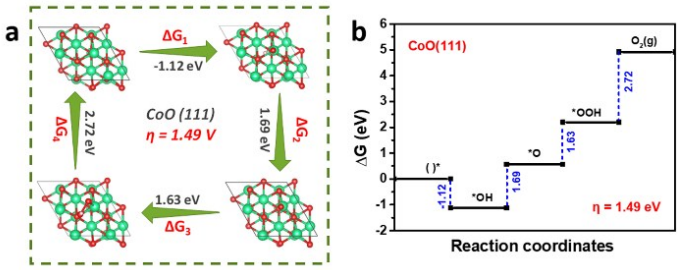

Fig. S14 (a) Adsorption configurations over the (111) plane of CoO. (b) The calculated OER free energy diagram over the (111) plane of CoO.