

Supporting Information

Co/CoO Hybrid Rooted on Carbon Cloth as An Efficient Electrocatalyst for Hydrogen Evolution Reaction under Alkaline Solution

Jun Cao ^a, Xiaobin Chen ^b, Haichao Li ^a, Jiaxuan Pu ^b, Limei Liu ^c, Li Ma ^a, Kechao Zhou
^a, Zejie Zhang ^a, Qiuping Wei ^{b, **, *}, Fenghua Luo ^{a, *}

^a State Key Laboratory of Powder Metallurgy, Central South University, Changsha
410083, PR China

^b School of Materials Science and Engineering, Central South University, Changsha
410083, PR China

^c Jiaxing Super Lighting Electric Appliance Co., Ltd., Jiaxing, China.

* E-mail: fenghualuo@csu.edu.cn (F. H. Luo); qiupwei@csu.edu.cn (Q. P. Wei)

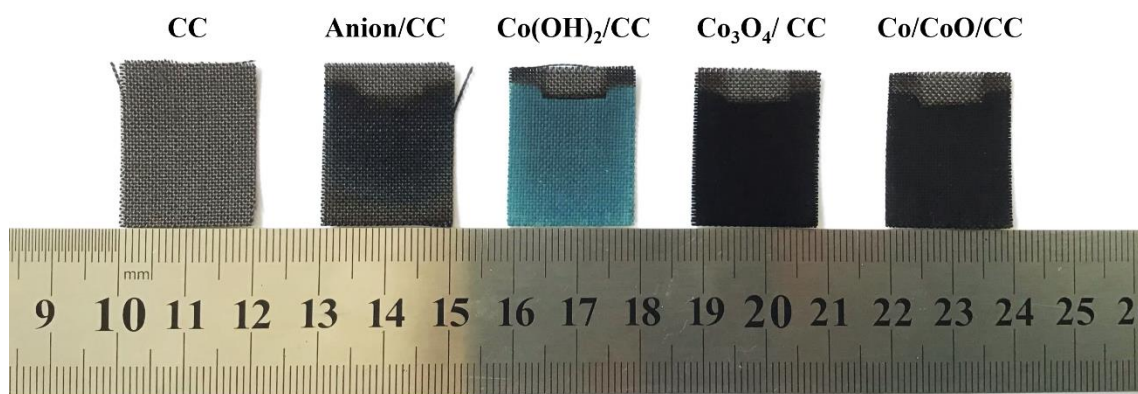


Fig. S1 the photos of prepared samples.

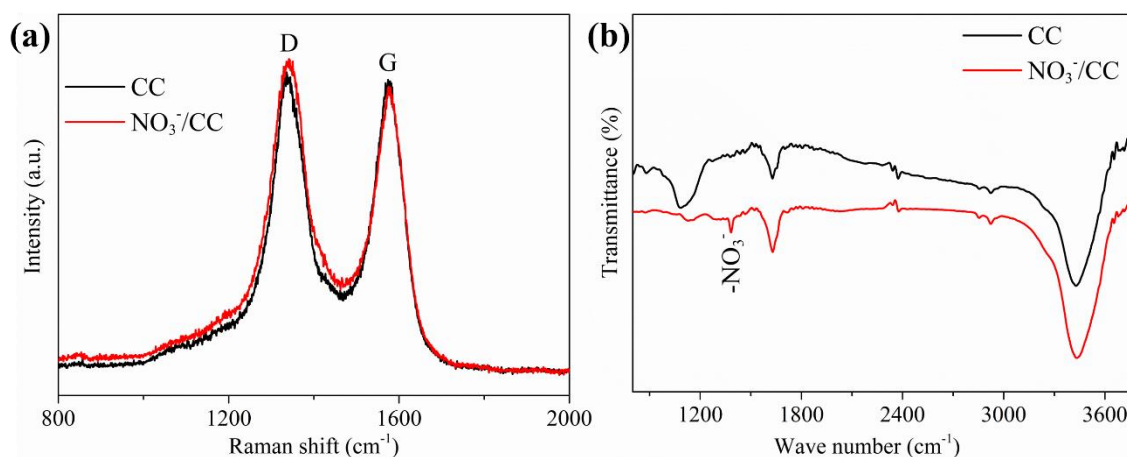


Fig. S2 the Raman spectra (a), FTIR spectrum (b) of CC and NO₃⁻ embedded CC.

The CC was first subjected to anodic oxidation in 0.1 M KNO₃ for 600 s at 10 mA/cm² and then rinsed thoroughly water to remove the surface-adsorbed nitrate. As shown in Fig. S2a, the intensity of D band peak of nitrate-inserted CC exhibits higher than that of pristine CC, indicating that more defects are presented in CC after anion inserted^{1,2}. Moreover, as observed in Fig. S2b, the FTIR spectrum of treated CC displays an apparent peak at 1384 cm⁻¹ assignable to the asymmetric stretching vibration of nitrate functional groups³, indicating that the nitrate anions were successfully inserted into CC.

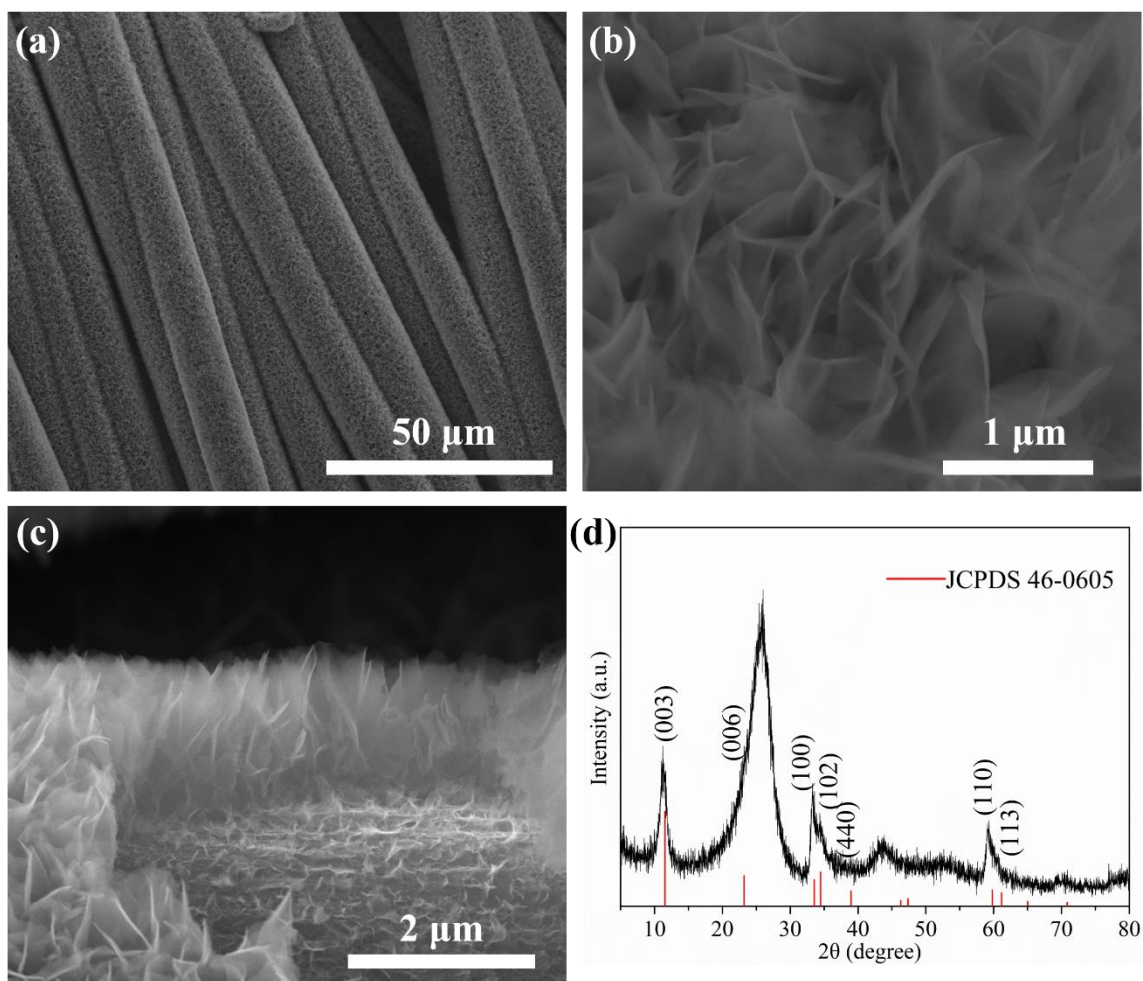


Fig. S3 the SEM images (a-c) and XRD pattern (d) of Co(OH)_2 electrodeposited on CC with NO_3^- intercalation.

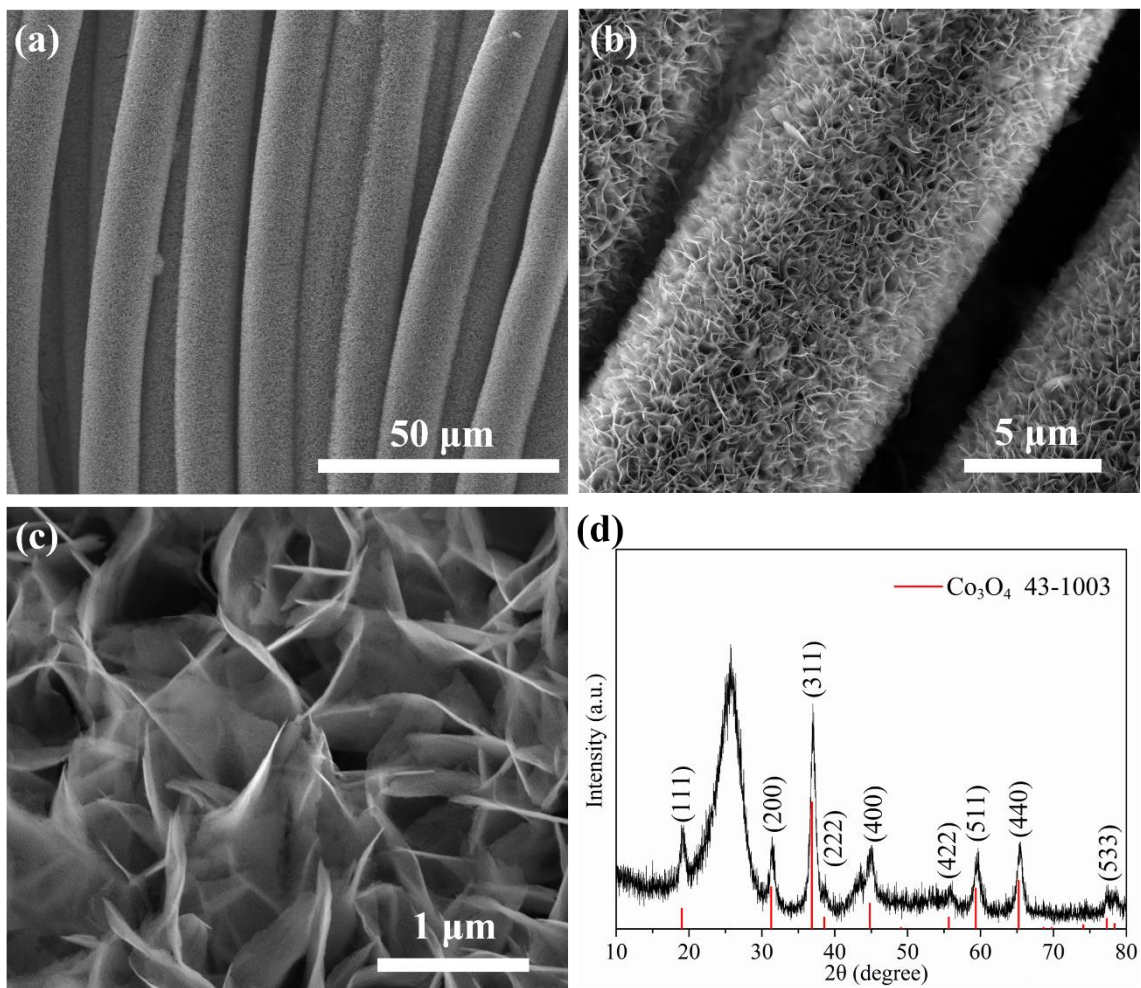


Fig. S4 the SEM images (a-c) and XRD pattern (d) of $\text{Co}_3\text{O}_4/\text{CC}$.

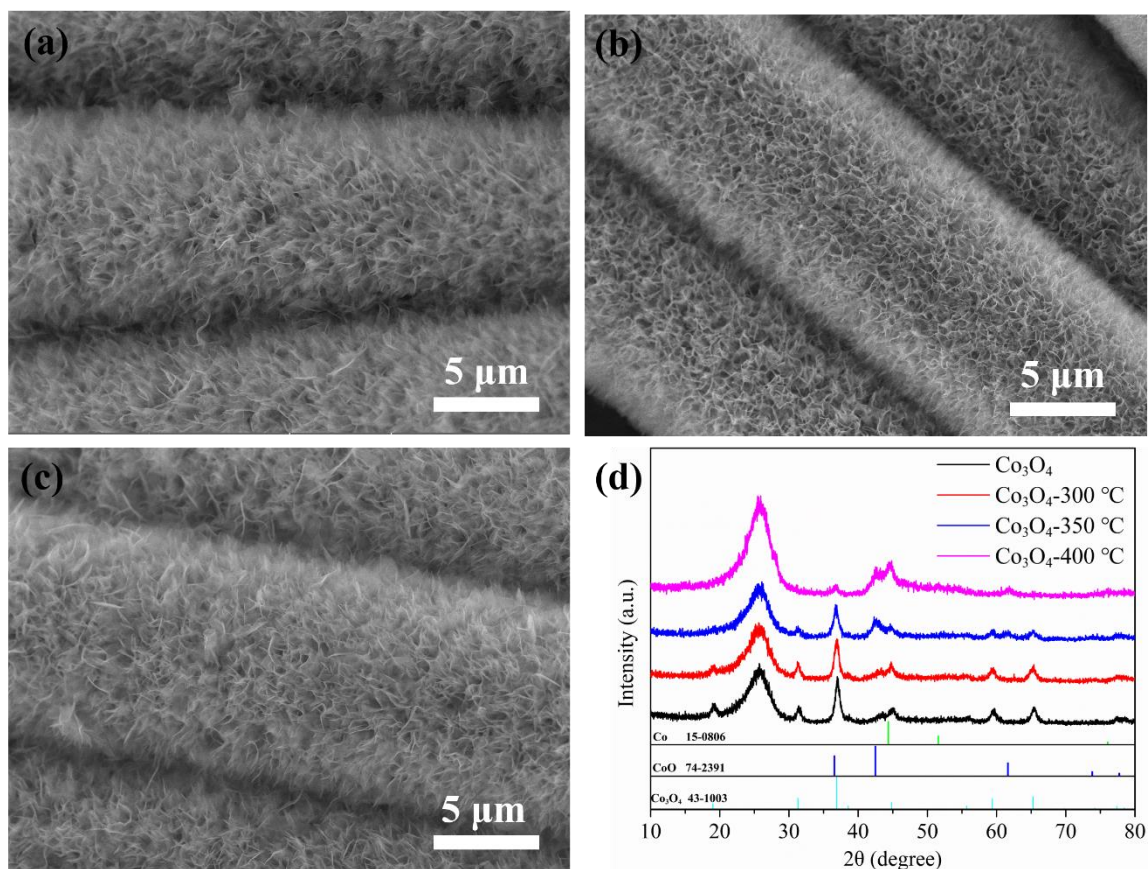


Fig. S5 SEM low magnification images of Co/CoO-10 (a), Co/CoO-30 (b), Co/CoO-50 (c); XRD patterns of products derived from Co_3O_4 reduced at different temperature in 10% H_2/Ar atmosphere for 4h.

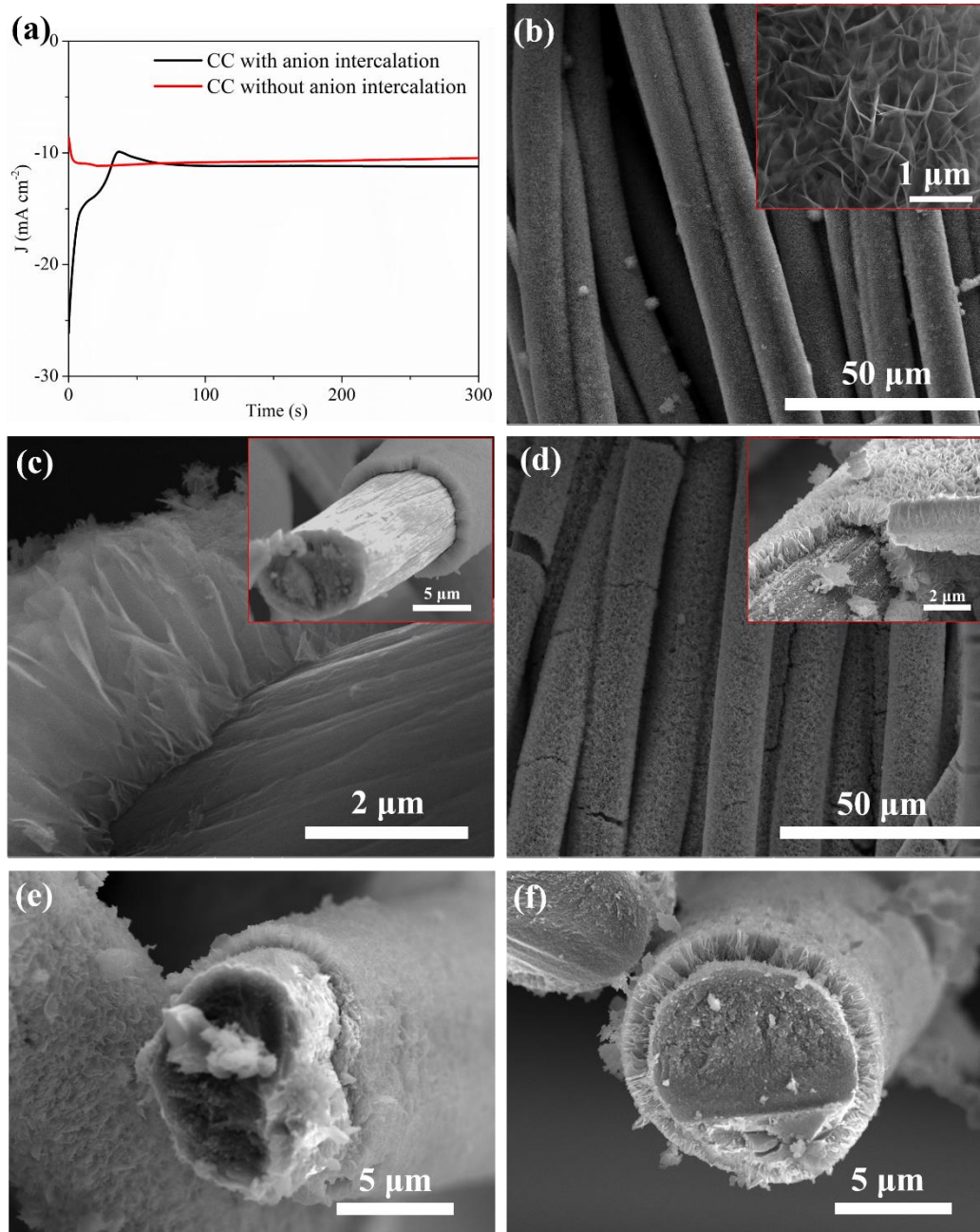


Fig. S6 (a) the curves of current density versus time for Co(OH)₂ electrodeposited on CC; (b) SEM image of Co(OH)₂ coated on CC without pre-anion insertion (the inset is the high magnification image); (c) SEM image of gap between film and CC without intercalation (the inset is the cross section of single carbon fiber); (d) SEM image of Co₃O₄ covered on CC without anion intercalation after calcination at air (the inset is a representative single fiber); (e) the cross section of Co(OH)₂ film on CC with anion insertion; (f) the cross section of Co₃O₄ film on CC with anion insertion

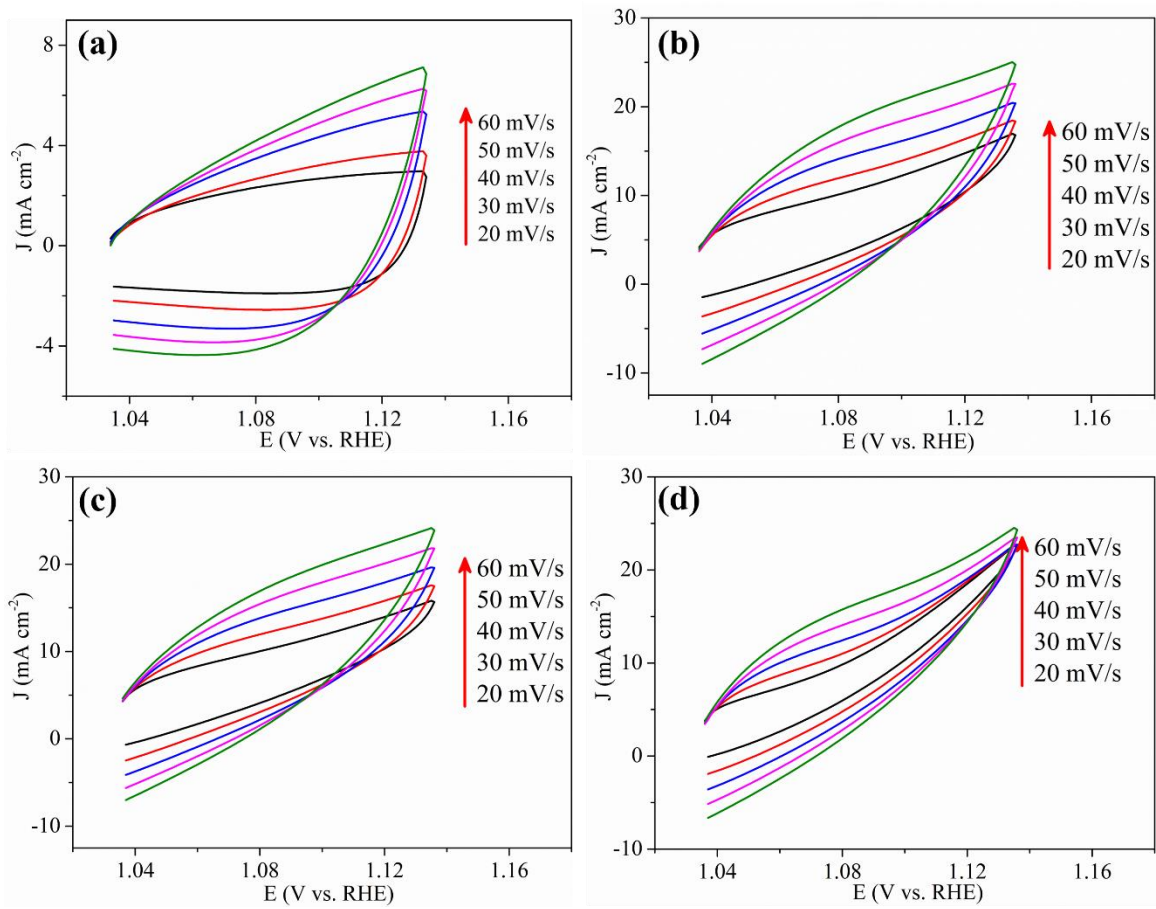


Fig. S7 the CV curves of various samples scanned at different rates between +1.036 V and +1.136 V: (a) Co_3O_4 , (b) Co/CoO -10, (c) Co/CoO -30 and (d) Co/CoO -50.

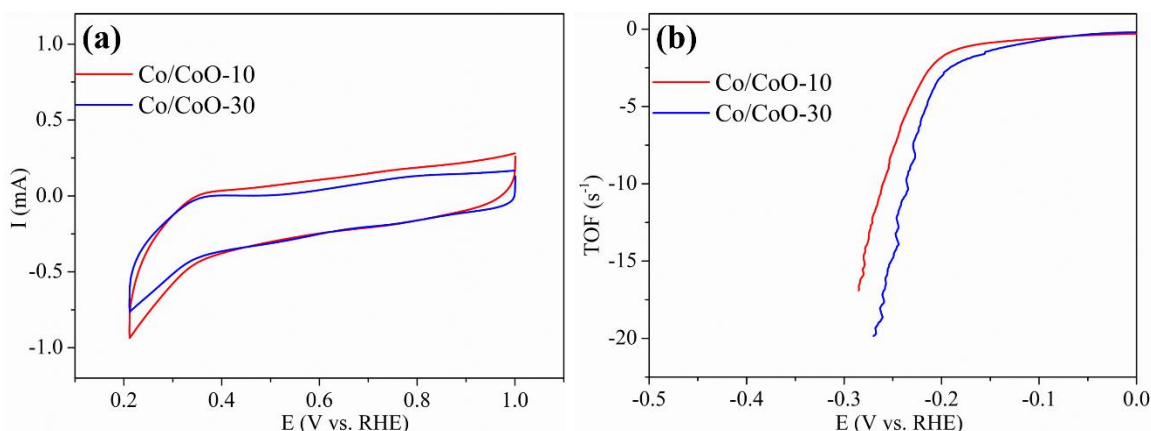


Fig. S8 (a) CV curves of Co/CoO-10 and Co/CoO-30 recorded between 0.22V and 1.0 V (vs RHE) in 0.1 M PBS (pH=7) with a scan rate of 50 mV/s. (b) comparison of TOFs values of Co/CoO-10 and Co/CoO-30.

The TOFs (s⁻¹) for HER were calculated with the following equation^{4, 5}:

$$TOF = \frac{I}{2NF}$$

I: the current recorded in LSV measurement.

The factor 1/2 arrives by taking into account that two electrons are required for forming one hydrogen molecule from two protons.

N: the active sites of various catalysts (in mol), CV measurements carried out in 0.1 M PBS electrolyte (pH=7) with a scan rate of 50 mV/s at the potential windows from 0.22 to 1.0V (vs RHE). The absolute components of the voltammetric charges (cathodic and anodic) tested during one CV cycle were calculated. Assuming one electron redox process, the integrated charge over the whole potential range is divided by two. Then the value was divided by the Faraday constant to obtain the number of active sites for different electrode.

F: Faraday constant (in C/mol).

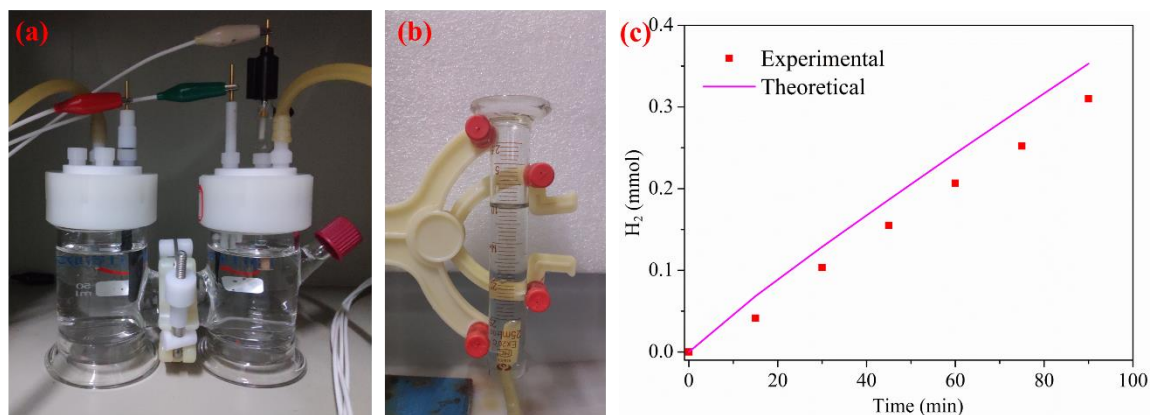


Fig. S9 (a, b) Detail of faradic efficiency measurement of the Co/CoO-30. (c) Amounts of theoretical and experimental hydrogen (H₂)

The Faradaic efficiency (FE) is calculated based on the following formula^{6, 7}:

$$FE = (V/V_m)/(Q/(n \times F))$$

In where, V is the volume of gas evolved during test. V_m is the molar volume (24.2 L mol⁻¹, 288.5 K), Q is total quantity of electric charge (C), F is the Faradic constant (96485.3 C mol⁻¹) and n is the number of moles of electrons transferred during the reaction while it is generating 1 mol for gas (which is 2 for H₂).

By comparing the amount of theoretically calculated H₂ with the experimentally measured quantities, it was found that the faradic efficiency (87.7%) was a little far from unity during initial 1.5 h test, indicating the consumption of partial charges for parasitic reactions.

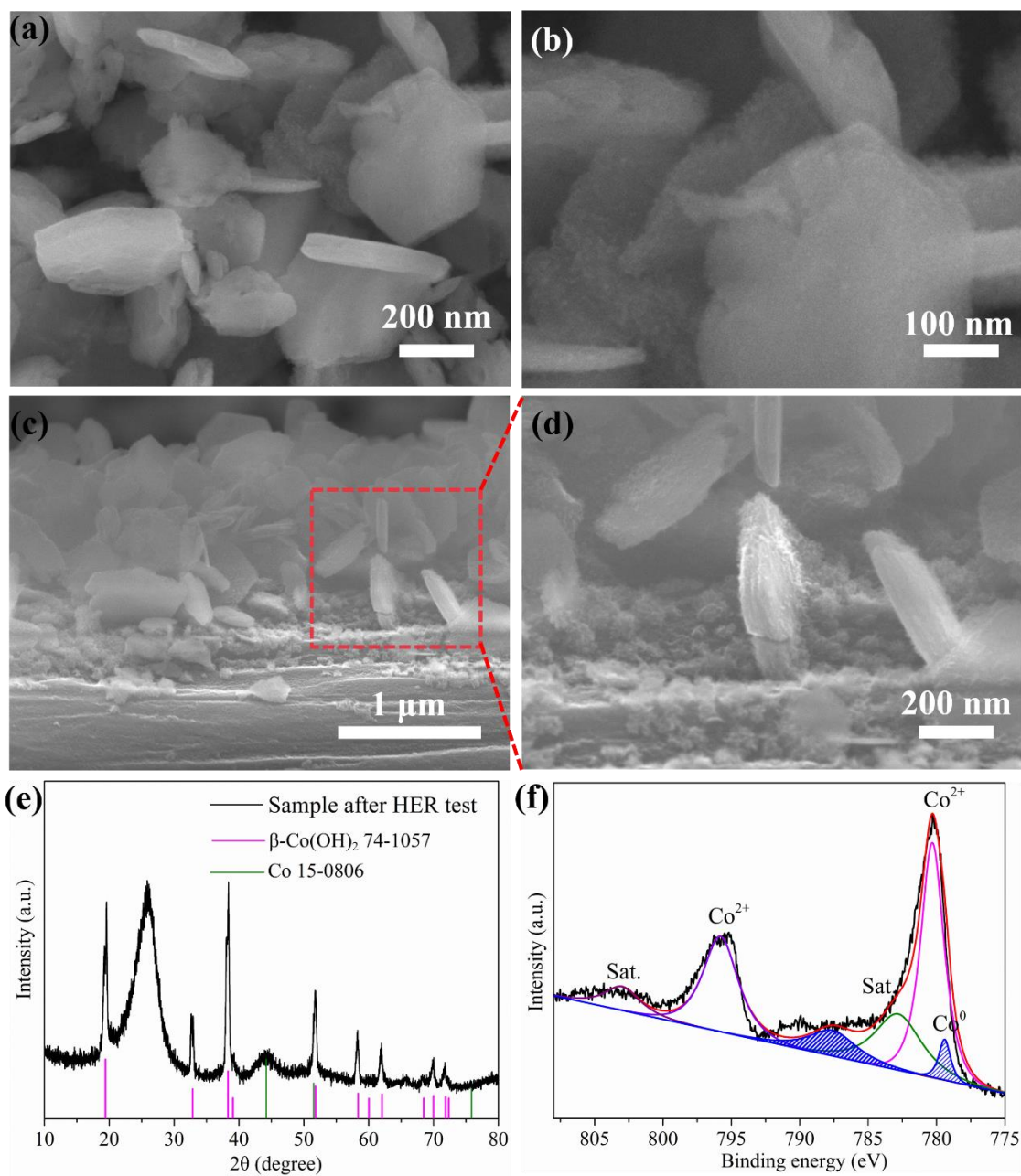


Fig. S10 (a-b) SEM images, (b-c) SEM images from side view, (d) XRD pattern of the sample (Co/CoO-30) after HER test.

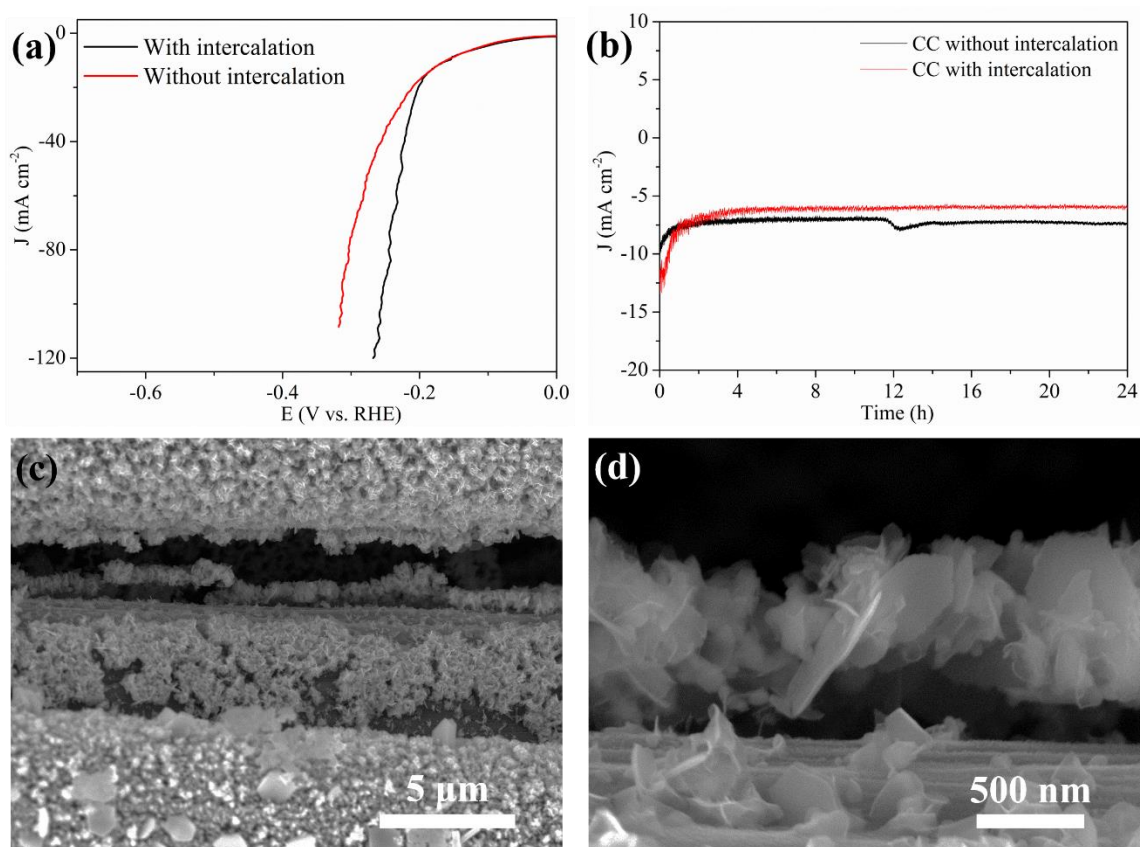


Fig. S11 (a) The performance of Co/CoO-30 load on CC with intercalation and without intercalation: (a) LSV curves; (b) Durability test at constant-voltage (-248 mV for CC with intercalation and -208 mV for CC without intercalation); (c-d) The low and magnified SEM images of Co/CoO-30 coated on CC without intercalation after long-term stability test.

Table S1 Comparison of HER Activities for Different catalysts.

Catalysts	Solutions	$\eta@10\text{mA}/\text{cm}^2$ (mV)	References
Co/CoO-30	1.0 M KOH	160	This work
CoO _x @CN	1.0 M KOH	232	8
CoO/MoO _x	1.0 M KOH	163	9
Co-MoS ₂	1.0 M KOH	230	10
A-PBCCF-H	1.0 M KOH	~270	11
Co@Co ₃ O ₄ -NC	1.0 M KOH	221	12
Co/CoP-5	1.0 M KOH	253	13
	0.5 M H ₂ SO ₄	178	
Co ₃ O ₄ @Ni	1.0 M KOH	225	14
Co/CoO (dark)	1.0 M KOH	232	15
CoO	1.0 M KOH	240	16
Co _{0.65} B _{0.3} NC800	1.0 M KOH	170	17
Co@NC--G-800	0.5 M H ₂ SO ₄	~210	18
	1.0 M KOH	~182	
Co-CoO@3DHPG	1.0 M KOH	402	19
Co ₃ O ₄ @MoS ₂	1.0 M KOH	205	20
NF/NiCoMoO-Ar	1.0 M KOH	181	21

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