

Supporting information

Ca²⁺ doped ultrathin cobalt hydroxyoxides from coordination polymers as efficient electrocatalysts for water oxidations

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Table S1 Electrochemical impedance spectroscopy (EIS) fitting results. R_s : electrolyte resistance, R_{CT} : charge-transfer resistance.

Catalysts	R_s /ohms	R_{CT} /ohms
Co-CPs	8.7	3.8
Co _{0.91} Ca _{0.09} -CPs	6.9	3.7
Co _{0.89} Ca _{0.11} -CPs	7.3	2.5
Co _{0.83} Ca _{0.17} -CPs	7.5	2.9

Table S2 Comparison of the OER performance of Co_{0.89}Ca_{0.11}-CPs with selected cobalt based catalysts from the literature. GC: glass carbon; NF: nickel foam.

Catalyst	Substrate	Electrolyte	$\eta@10 \text{ mA cm}^{-2}$ (V)	Tafel slopes (mV dec^{-1})	References
Co _{0.89} Ca _{0.11} -CPs	GC	1.0 M KOH	0.37	58.8	This work
2D Co-ZIF-9	GC	1.0 M KOH	0.38	55	Adv. Sci. 2018, 5, 1801029
CoP	NF	1.0 M KOH	0.39	65	Adv. Funct. Mater. 2015, 25, 7337
CoOx-ZIF ZIF-67	GC	1.0 M KOH	0.32 0.40	70.3 108.8	Adv. Funct. Mater. 2017, 27, 1702546
Co(OH) ₂ @NCNTs	NF	1.0 M KOH	0.27	72	Nano Energy, 2018, 47, 96
Co ₃ O ₄ film	Au	1.0 M KOH	0.39	61	Electrochimica Acta 2014, 140, 359.
Co@C-MWCNTs Co ₃ O ₄ @C-MWCNTs	GC	1.0 M KOH	0.32 0.39	67 62	J. Mater. Chem. A, 2015, 3, 17392
Co ₃ O ₄ /CNW-C	GC	1.0 M KOH	0.41	54	J. Mater. Chem. A, 2015, 3, 11615

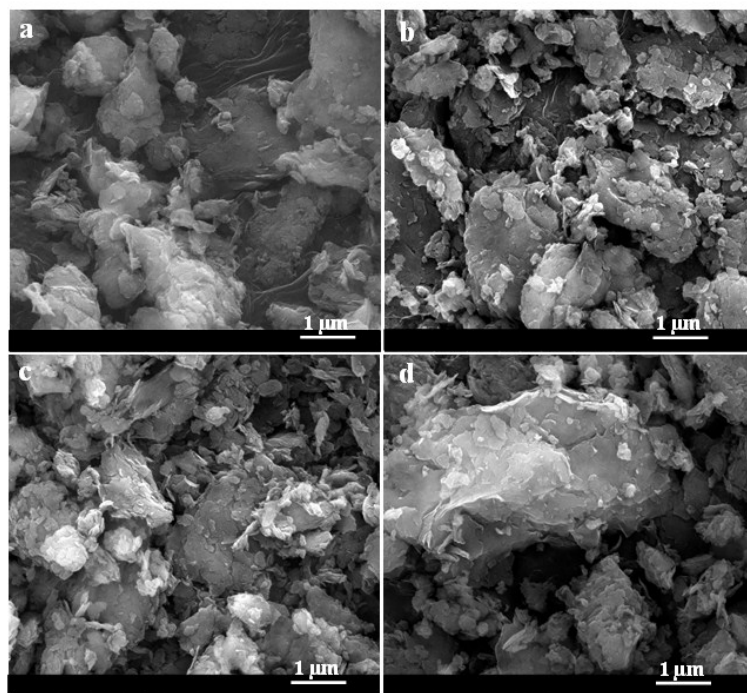


Fig. S1 SEM images of Co-CPs (a), $\text{Co}_{0.91}\text{Ca}_{0.09}$ -CPs (b), $\text{Co}_{0.89}\text{Ca}_{0.11}$ -CPs (c), and $\text{Co}_{0.83}\text{Ca}_{0.17}$ -CPs (d).

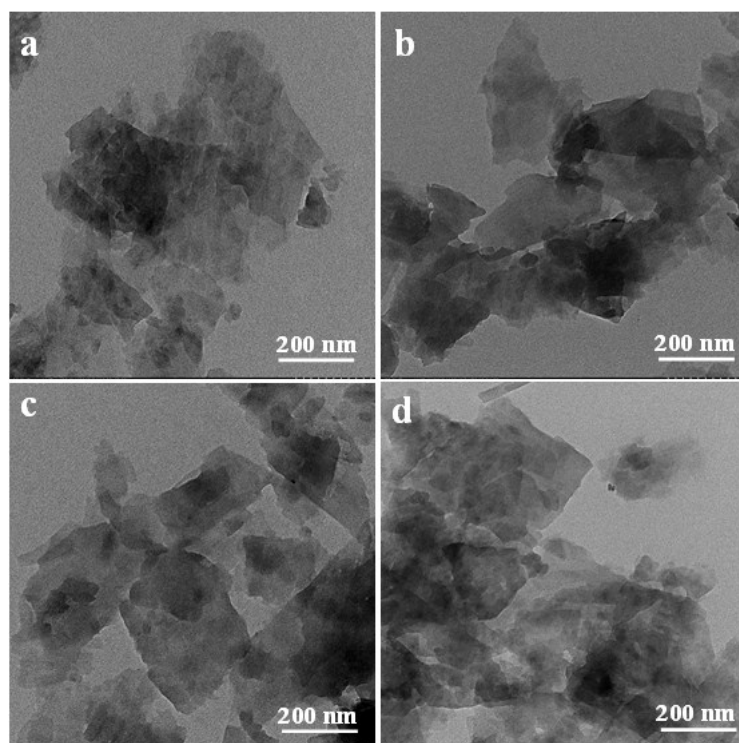


Fig. S2 TEM images of Co-CPs (a), $\text{Co}_{0.91}\text{Ca}_{0.09}$ -CPs (b), $\text{Co}_{0.89}\text{Ca}_{0.11}$ -CPs (c) and $\text{Co}_{0.83}\text{Ca}_{0.17}$ -CPs (d).

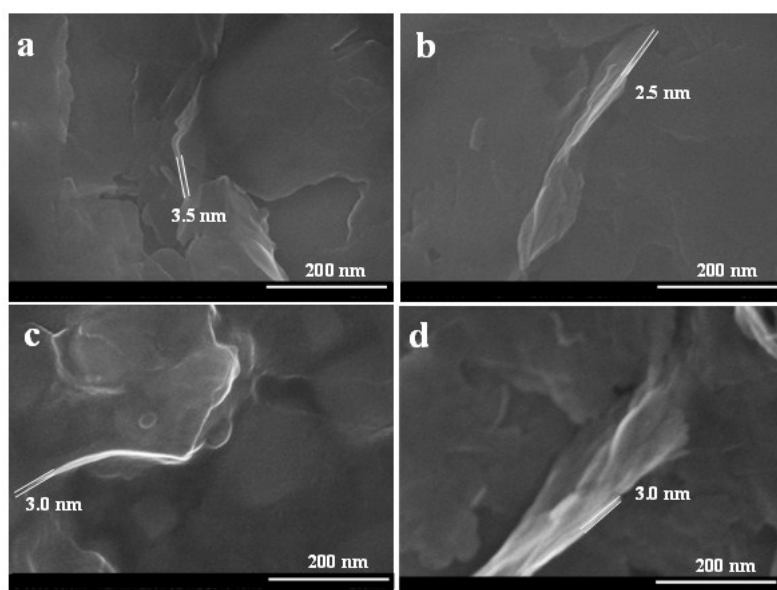


Fig. S3 HRSEM images of (a) Co-CPs, (b) $\text{Co}_{0.91}\text{Ca}_{0.09}$ -CPs, (c) $\text{Co}_{0.89}\text{Ca}_{0.11}$ -CPs and (d) $\text{Co}_{0.83}\text{Ca}_{0.17}$ -CPs.

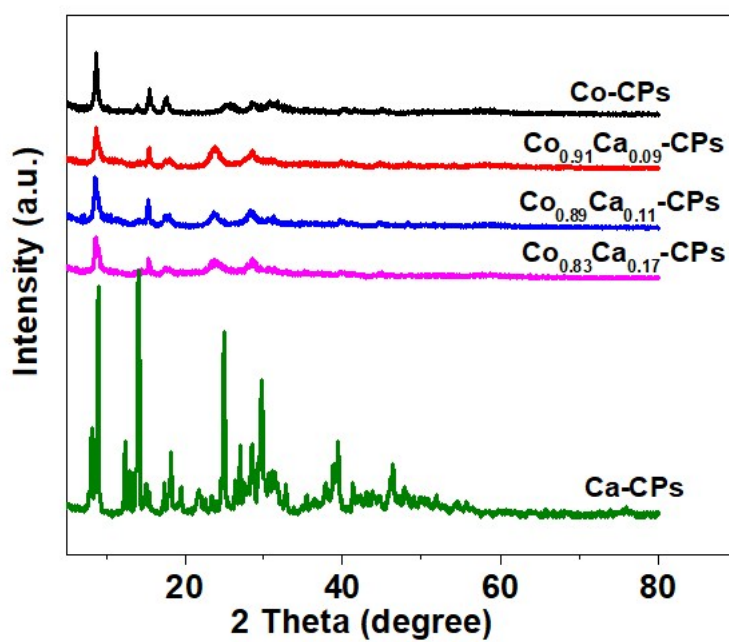


Fig. S4 XRD patterns of Co-CPs, Co_xCa_y -CPs and Ca-CPs.

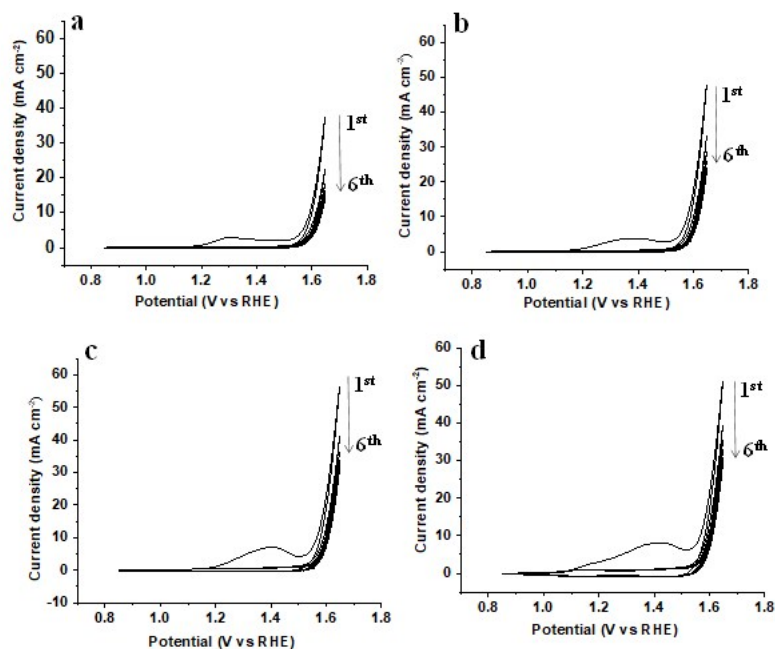


Fig. S5 Cyclic voltammetry (CV) curves without IR compensation during the potential range of 0.85V to 1.65V vs RHE in 1M KOH electrolyte for the catalysts: (a) Co-CPs, (b) $\text{Co}_{0.91}\text{Ca}_{0.09}$ -CPs, (c) $\text{Co}_{0.89}\text{Ca}_{0.11}$ -CPs and (d) $\text{Co}_{0.83}\text{Ca}_{0.17}$ -CPs.

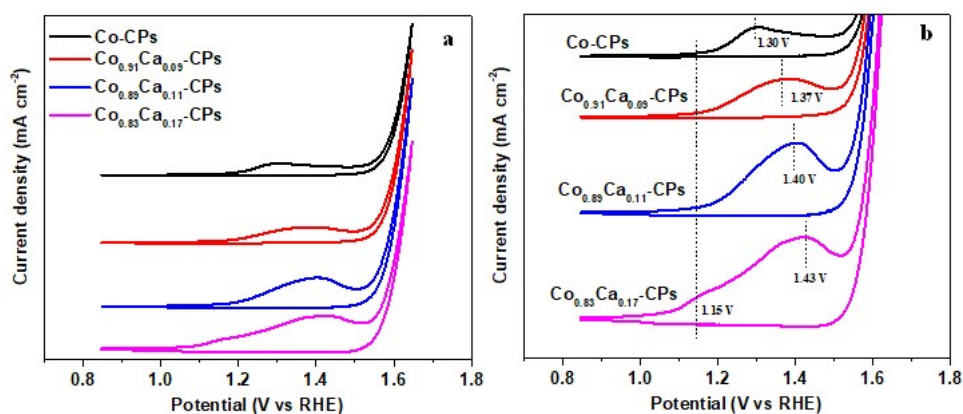


Fig. S6 The first CV curves for Co-CPs and Co_xCa_y -CPs in 1 M KOH electrolyte.

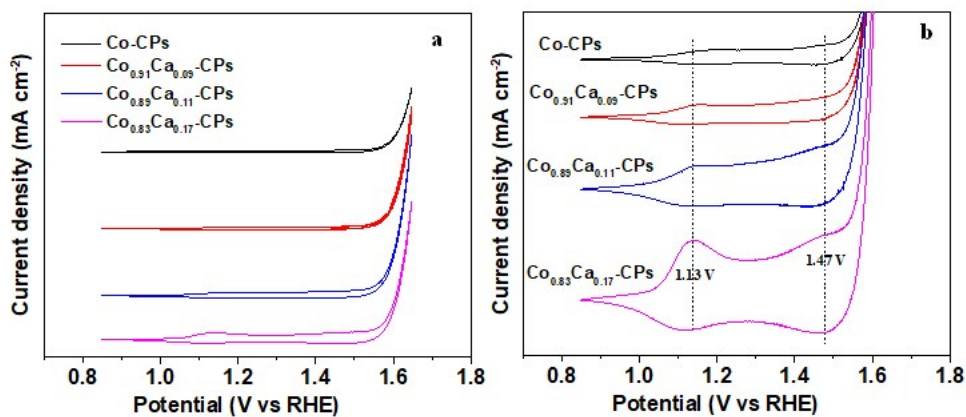


Fig. S7 The stable CV curves for Co-CPs and Co_xCa_y -CPs in 1 M KOH electrolyte.

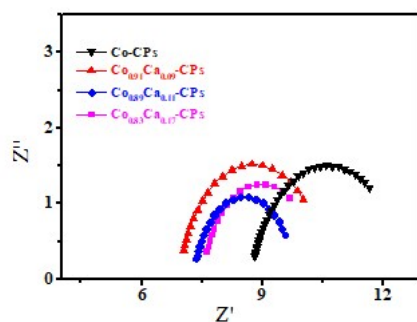


Fig. S8 EIS of anodic oxidized products of Co-CPs and Co_xCa_y -CPs measured at a constant potential of 1.55 V versus RHE.

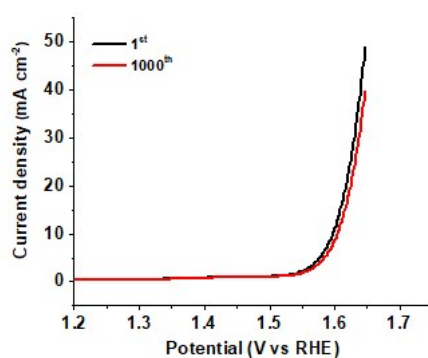
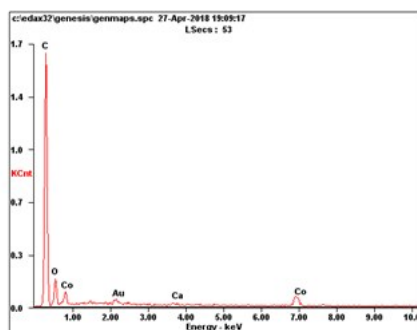
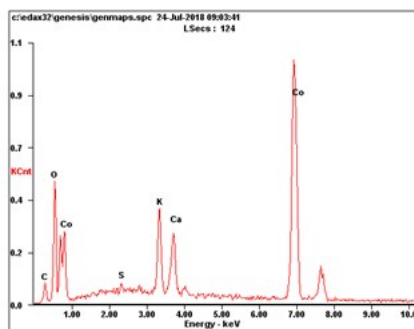


Fig. S9 LSV polarization curves of $\text{Co}_{0.89}\text{Ca}_{0.11}$ -CPs before and after cycling for 1000 cycles.



Element	Wt%	At%
CK	79.70	87.22
OK	14.15	11.63
AuM	01.61	00.11
CaK	00.34	00.11
CoK	04.19	00.93
Matrix	Correction	ZAF

Fig. S10 EDS result of $\text{Co}_{0.89}\text{Ca}_{0.11}$ -CPs before OER stability test.



Element	Wt%	At%
CK	09.37	23.29
OK	20.30	37.88
SK	00.71	00.66
KK	06.55	05.00
CaK	05.13	03.82
CoK	57.94	29.35
Matrix	Correction	ZAF

Fig. S11 EDS result of $\text{Co}_{0.89}\text{Ca}_{0.11}$ -CPs after OER stability test.

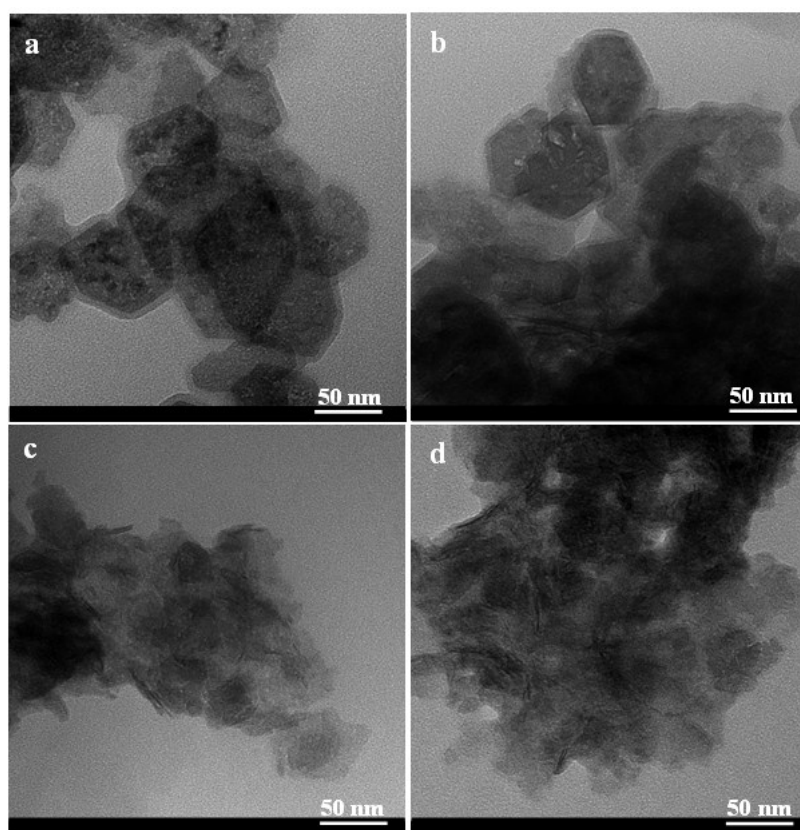


Fig. S12 TEM images of anodic oxidized products of Co-CPs (a), $\text{Co}_{0.91}\text{Ca}_{0.09}$ -CPs (b), $\text{Co}_{0.89}\text{Ca}_{0.11}$ -CPs (c) and $\text{Co}_{0.83}\text{Ca}_{0.17}$ -CPs (d) in 1.0 M KOH aqueous electrolyte.

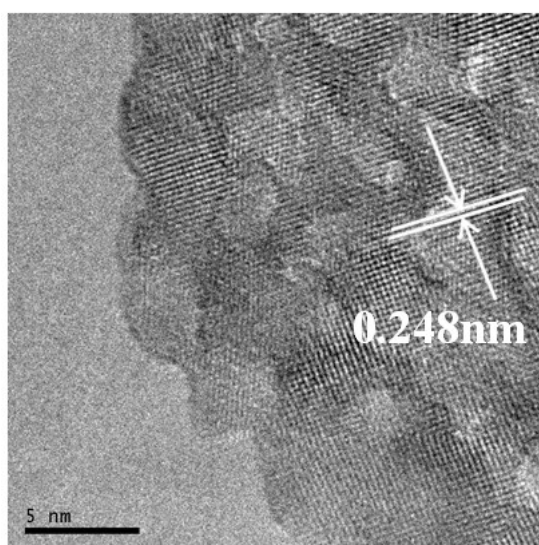


Fig. S13 HRTEM image of anodic oxidized product of Co-CPs after OER.

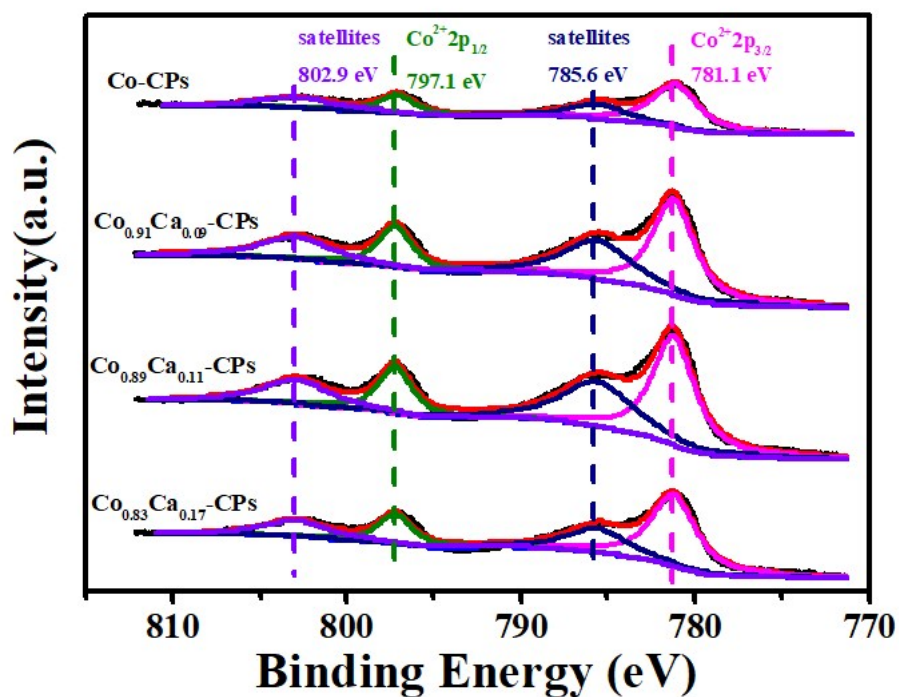


Fig. S14 XPS spectra of Co-2p of Co-CPs and $\text{Co}_x\text{Ca}_y\text{-CPs}$.

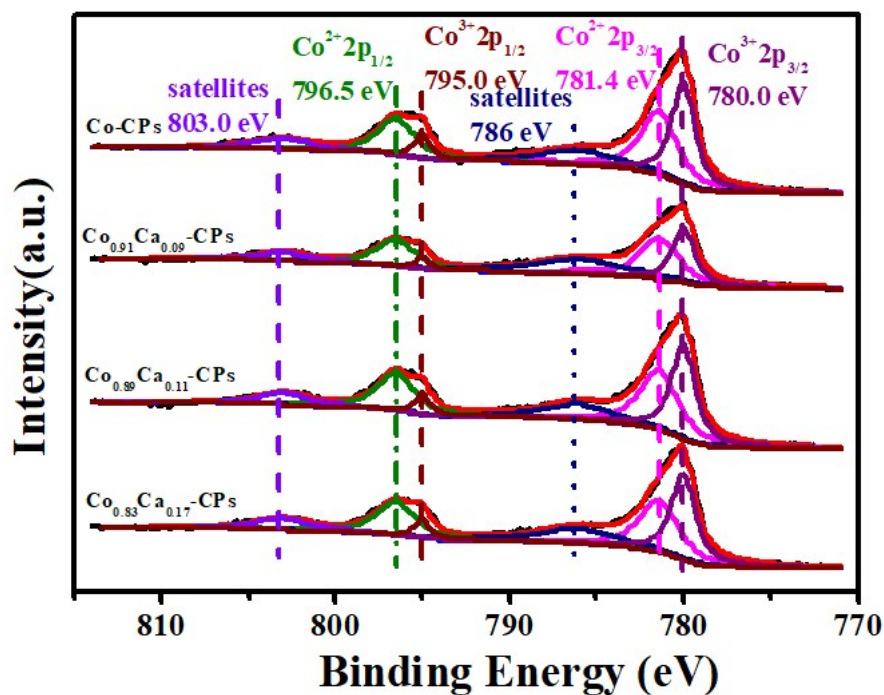


Fig. S15 XPS spectra of Co-2p for hydrolyzed samples of Co-CPs and $\text{Co}_x\text{Ca}_y\text{-CPs}$ in 1 M KOH.

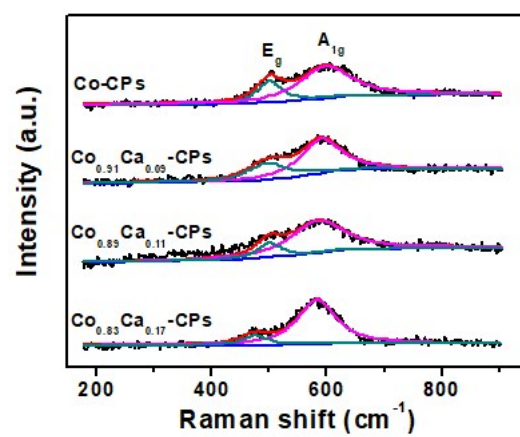


Fig. S16 Raman spectra of the anodic oxidized products of Co-CPs and Co_xCa_y-CPs after OER.