Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Boride-Mediated Synthesis of Highly Active Cobalt-Based Electrocatalyst for Alkaline Hydrogen Evolution Reaction

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Chemicals and Materials: The cobalt foam (CF, ≥ 99.0% purity) with a thickness of 1.80 mm, an area density of about 650 g·m^{-2} and an average pore size of 0.25–0.80 mm was purchased from Incoatm. Cobalt sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$, 99.5%, Macklin), dimethylamine borane (DMAB, 96.0%, Macklin), disodium succinate ($C_4H_4Na_2O_4$, 99.0%, Macklin), potassium hydroxide (KOH, 95.0%, Macklin), Pt/C (20 wt% Pt on Vulcan XC-72R, Macklin), nafion solution (5 wt% in mixture of lower aliphatic alcohols and water, Sigma-Aldrich), cobalt powder (Co, 99.9%, Aladdin), boron powder (B, 98.0%, Macklin) and other reagents of analytical grade were all obtained from commercial sources and used without further purification. Deionized (DI) water was used throughout the experiments.

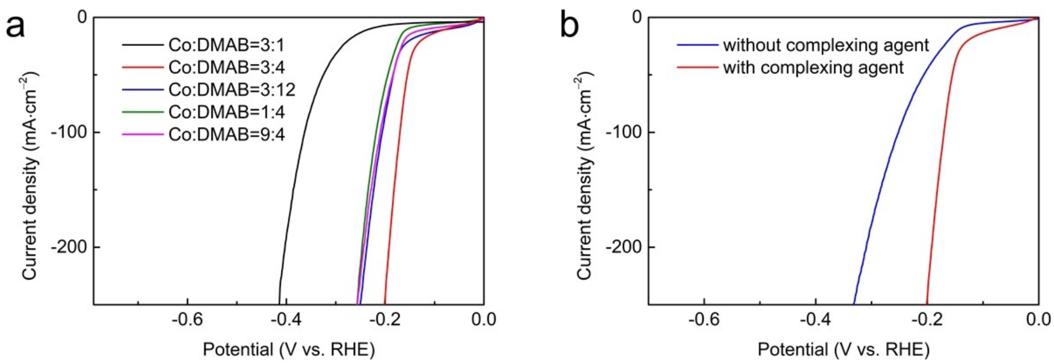

Figure S1. HER polarization curves (with 95% iR compensation) of the $Co_2B/CoO/H_3BO_3$/CF catalysts that were prepared using reduction solution (a) with different Co/DMAB molar ratios, (b) with and without complexing agent and Co/DMAB molar ratio was fixed at 3:4.

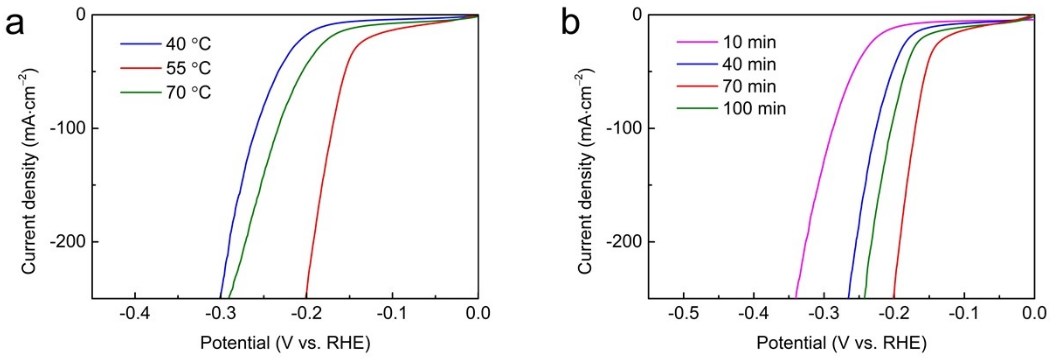

Figure S2. HER polarization curves (with 95% iR compensation) of the $Co_2B/CoO/H_3BO_3/CF$ catalysts that were prepared (a) at different reduction temperatures in the presence of $C_4H_4Na_2O_4$ and a fixed Co/DMAB molar ratio of 3:4; (b) at 55 °C in the presence of $C_4H_4Na_2O_4$ and a fixed Co/DMAB molar ratio of 3:4 with different reduction times.

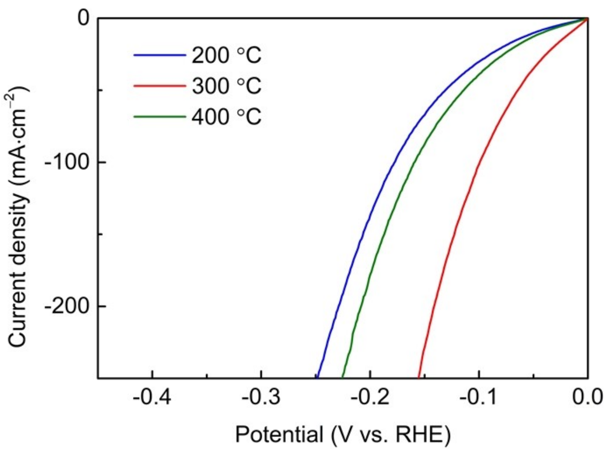

Figure S3. HER polarization curves (with 95% iR compensation) of the $Co_2B/CoO/H_3BO_3/CF$ catalysts that were prepared at 55 °C for 70 min in the presence of $C_4H_4Na_2O_4$ and a fixed Co/DMAB molar ratio of 3:4 with different annealing temperatures.

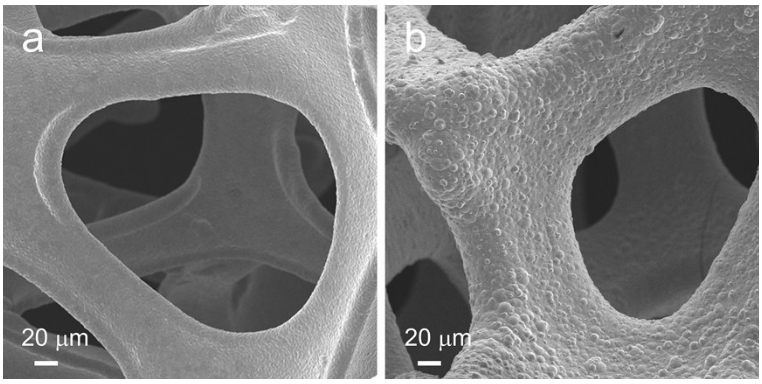

Figure S4. FE-SEM images of (a) CF and (b) $Co_2B/CoO/H_3BO_3$/CF at low magnification.

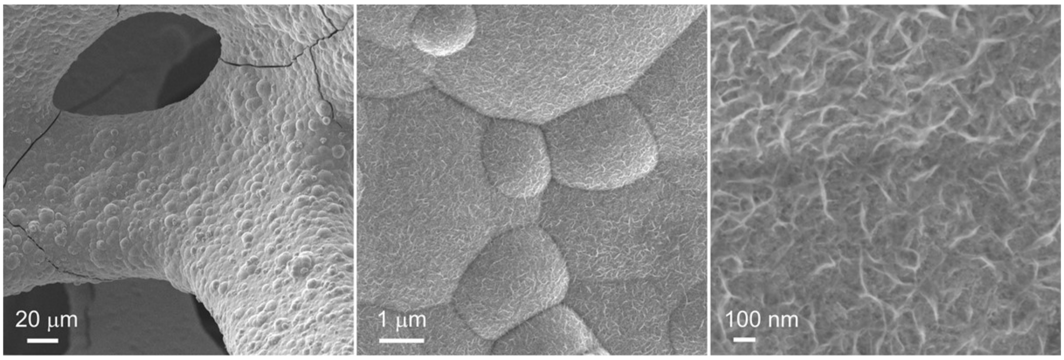

Figure S5. FE-SEM images of $Co/CoO/B_2O_3/CF$ at different magnifications.

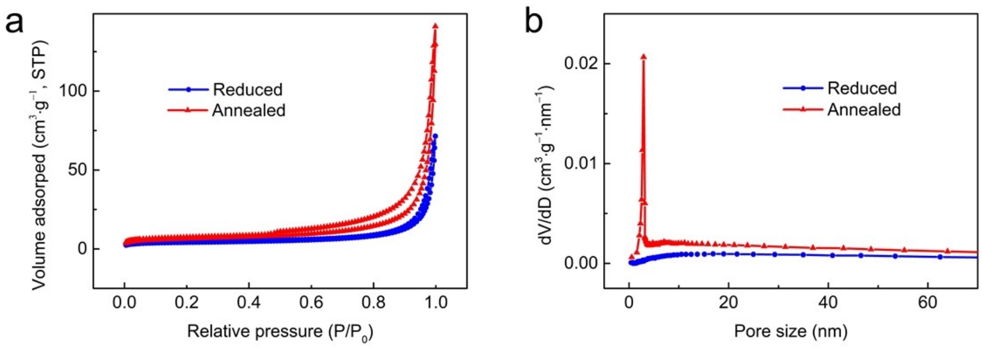

Figure S6. (a) N_2 adsorption-desorption isotherms and (b) the corresponding pore size distributions of the reduced and annealed samples.

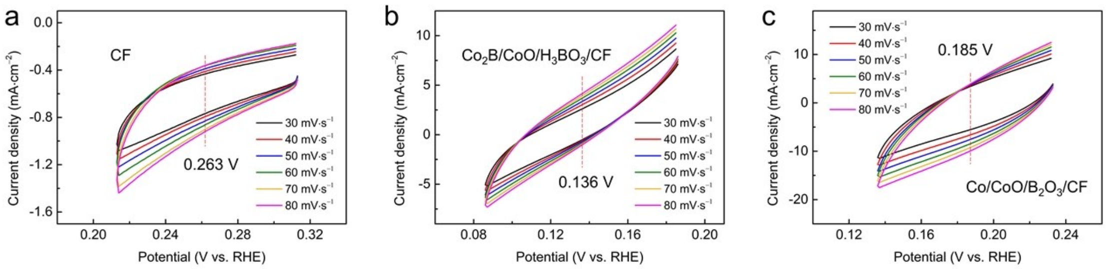

Figure S7. CV curves of (a) CF, (b) $Co_2B/CoO/H_3BO_3/CF$ and (c) $Co/CoO/B_2O_3/CF$ catalysts at varied scan rates.

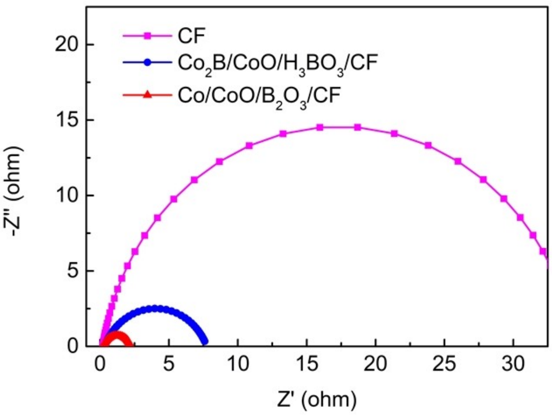

Figure S8. EIS Nyquist plots of various electrocatalysts at open-circuit potential.

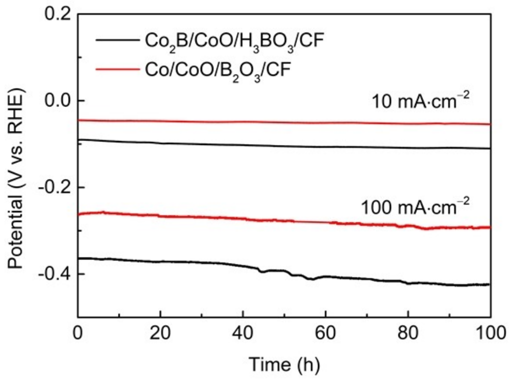

Figure S9. Chronopotentiometric curves of the $Co_2B/CoO/H_3BO_3/CF$ and $Co/CoO/B_2O_3/CF$ catalysts at 10 and 100 mA·cm^{-2}, respectively.

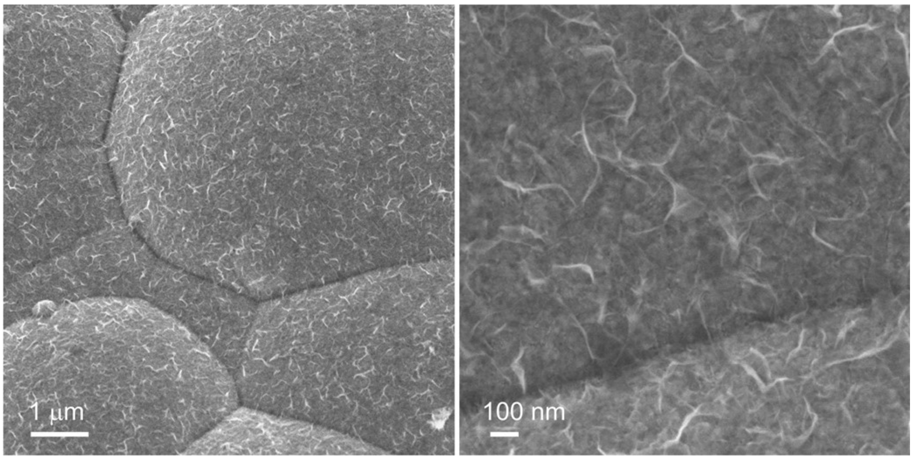

Figure S10. FE-SEM images of the post-used $Co/CoO/B_2O_3/CF$ catalyst after 100 h of durability test.

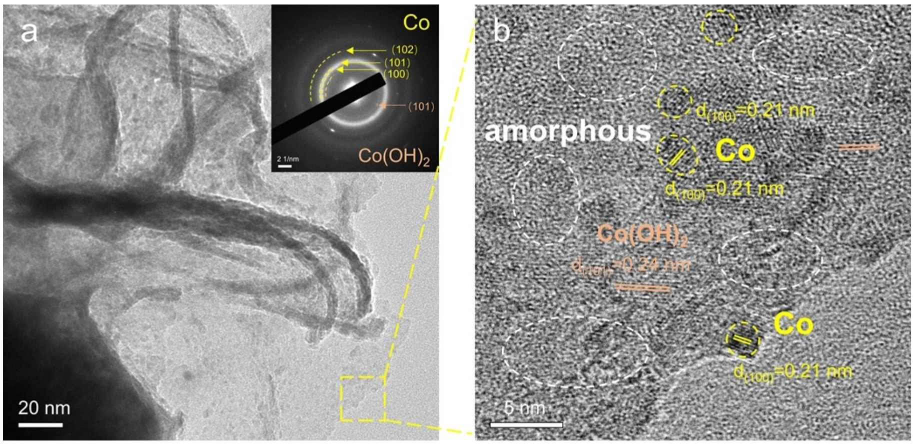

Figure S11. (a) TEM image and the corresponding SAED pattern (inset) and (b) HRTEM image of the post-used Co/CoO/B_2O_3/CF catalyst after 100 h of durability test.

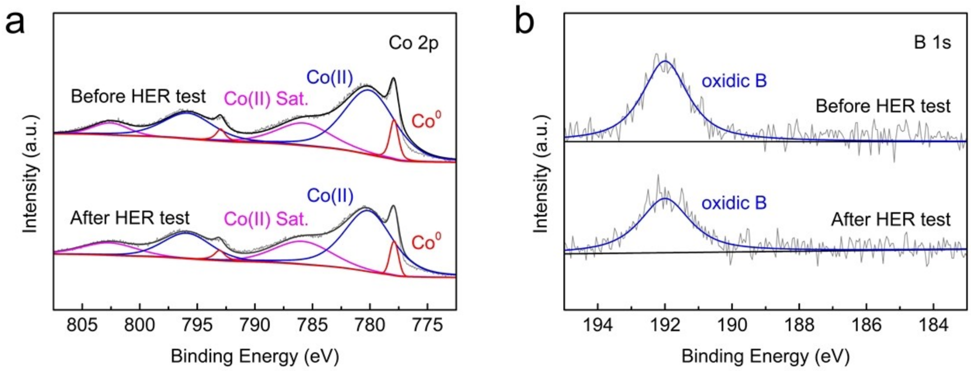

Figure S12. XPS spectra of the $Co/CoO/B_2O_3/CF$ catalysts before and after 100 h of durability test.

Table S1. A comparison of the HER performances of representative non-precious metal catalysts in a 1.0 M aqueous KOH electrolyte.

Electrocatalyst	Overpotential @10 $mA \cdot cm^{-2}$ (mV)	Overpotential @100 $mA \cdot cm^{-2}$ (mV)	Tafel slope ($mV \cdot dec^{-1}$)	Reference
O-NiCu	23	69	34.1	[1]
$Co/Co_2Mo_3O_8/NF$	25	113	33	[2]
$Co_2N/CoN/Co_2Mo_3O_8/CF$	25	90	28	[3]
C-$Ni_{1-x}O$	27	–	36	[4]
R-CoC_2O_4@MXene	28	65	43	[5]
C-Co_2P	30	65	36.9	[6]
Co@CoO/NF	76	–	81	[7]
Co-B-P/NF	42	88	42.1	[8]
Co-Mo-B/$CoMoO_{4-x}$/NF	56	172	66	[9]
Co-B@CoO/Ti	61	141	78	[10]
Co-B/Ni	70	210	67	[11]
Co-Mo-B/Ti	71	196	125	[12]
CoB/NF	110	219	96	[13]
$Co_2B/CoO/H_3BO_3/CF$	76	169	65	This work
$Co/CoO/B_2O_3/CF$	16	100	31	This work

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