Electronic Supplementary Information

Electrodeposited Amorphous Co-P-B Ternary Catalyst for Hydrogen Evolution

Reaction

Junhyeong Kim,^a Hyunki Kim,^a Soo-Kil Kim^{*b} and Sang Hyun Ahn^{**a}

^aSchool of Chemical Engineering and Material Science, Chung-Ang University, 84 Heukseokno, Dongjak-gu, Seoul, 06974, Republic of Korea ^bSchool of Integrative Engineering, Chung-Ang University, 84 Heukseokno, Dongjak-gu, Seoul, 06974, Republic of Korea

Corresponding authors

*Tel: +82-2-820-5770; Fax: +82-2-814-2651; E-mail: <u>sookilkim@cau.ac.kr</u>

**Tel: +82-2-820-5287; Fax: +82-2-824-3495; E-mail: <u>shahn@cau.ac.kr</u>

Catalyst	Electrolyte concentration (mM)				Atomic ratio ^a (%)		
	CoCl₂·6H₂O	NaH ₂ PO ₂ ·H ₂ O	H ₃ BO ₃	NaCl	Co	Р	В
Co ₇₇ P ₂₃ /CP		500	0		77.08	22.92	0.00
Co ₅₇ P ₂₇ B ₁₆ /CP		400	100		56.85	26.93	16.22
Co ₅₃ P ₂₇ B ₂₀ /CP		300	200		53.41	27.15	19.44
$Co_{59}P_{20}B_{21}/CP$	1	250	250	100	59.35	19.68	20.97
$Co_{41}P_{21}B_{38}/CP$		200	300		40.56	21.25	38.19
Co ₃₄ P ₂₀ B ₄₆ /CP		100	400		33.65	19.60	46.75
$Co_{89}B_{11}/CP$		0	500		88.62	0.00	11.38

Table S1. The concentration of the electrolyte for the Co-P-B catalysts electrodeposition in this experiment and its corresponding atomic ratio

a: Atomic ratio of each Co-P-B catalyst was measured using XPS analysis.

Catalyst	Overpotential at –10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Exchange current density (mA cm ⁻²)	Double layer capacitance (µF cm ⁻²)
Co ₇₇ P ₂₃ /CP	381	140	0.017	54.77
$Co_{57}P_{27}B_{16}/CP$	201	67	0.006	156.48
$Co_{53}P_{27}B_{20}/CP$	184	62	0.015	230.69
$Co_{59}P_{20}B_{21}/CP$	172	68	0.031	210.67
$Co_{41}P_{21}B_{38}/CP$	177	66	0.022	250.72
$Co_{34}P_{20}B_{46}/CP$	183	65	0.016	271.33
Co ₈₉ B ₁₁ /CP	438	157	0.016	30.27

Table S2. Electrochemical properties of Co-P-B catalyst with different atomic composition

	Catalyst	Co-P Ratio	Overpotential @ -10 mA cm ⁻² (mV)	Double layer capacitance (µF cm ⁻²)	Current density @ -0.15 V _{RHE} (mA cm ⁻²)	Scaled current @ -0.15 V _{RHE} (mA mF ⁻¹)
1	Co2P@NPG ^[64]	Co _{66.6} P _{33.3}	103	66,800	27.3	0.408
2	Co ₂ P/NCNTs ^[47]	Co _{66.6} P _{33.3}	150	5,700	10.1	1.771
3	CoP-OMC ^[32]	Co ₅₀ P ₅₀	112	22,720	29.8	1.311
4	CoP/CC ^[41]	Co ₅₀ P ₅₀	49	172,500	346	2.006
5	H-CoP/C ^[65]	Co ₅₀ P ₅₀	111	26500	95	3.584
6	u-CoP/Ti ^[66]	Co ₅₀ P ₅₀	45	86,000	341	3.965
7	CoP/NCNTs ^[47]	Co ₅₀ P ₅₀	79	16700	79	4.730
8	CoP UPNSs ^[67]	Co ₅₀ P ₅₀	56	7,870	157	19.949
9	CoP ₃ NWs/CFP ^[36]	Co ₂₅ P ₇₅	65	93,400	131	1.402
10	PCPTF ^[68]	Co _x P _y	153	3,800	9.8	2.579
This work	$Co_{59}P_{20}B_{21}/CP$	$Co_{59}P_{20}B_{21}$	172	210.67	4.849	23.017

Table S3. Comparison of electrochemical properties of $CoP_{0.33}B_{0.35}/CP$ in 0.5 M H_2SO_4 with other HER electrocatalysts



Fig. S1. Linear relationship between B/P ratio in electrolyte and B/P ratio in Co-P-B catalyst.



Fig. S2. Low- and (inset) high-magnification FESEM images of (a) $Co_{77}P_{23}/CP$ and (b) $Co_{89}B_{11}/CP.$



Figure S3. Double layer capacitance using cyclic voltammetry curves of (a) CP and Co-P-B catalysts in 0.5 M H_2SO_4 solution with different scan rates from 10 mV s⁻¹ to 200 mV s⁻¹: (b) Co₇₇P₂₃/CP, (c) Co₅₇P₂₇B₁₆/CP, (d) Co₅₃P₂₇B₂₀/CP, (e) Co59P₂₀B₂₁/CP, (f) Co₄₁P₂₁B₃₈/CP, (g) Co₃₄P₂₀B₄₆/CP, (h) Co₈₉B₁₁/CP.