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

Electronic Supplementary Information

Rhombic Porous CoP_2 Nanowire Arrays Synthesized by Alkaline Etching as Highly Active Hydrogen-Evolution-Reaction Electrocatalysts

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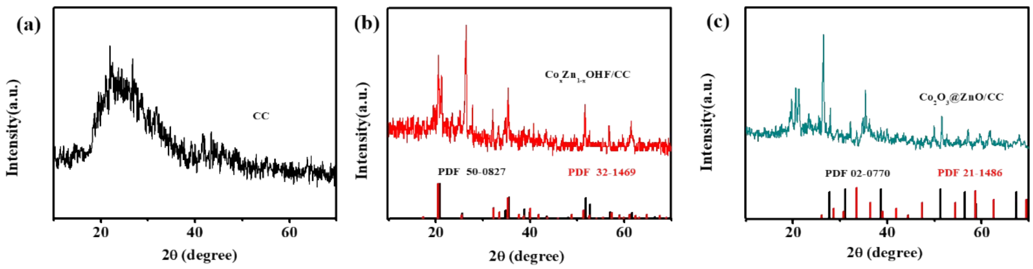

Fig. S1. XRD pattern of (a) CC; (b) $Co_xZn_{1-x}OHF/CC$; (c) $Co_2O_3@ZnO/CC$.

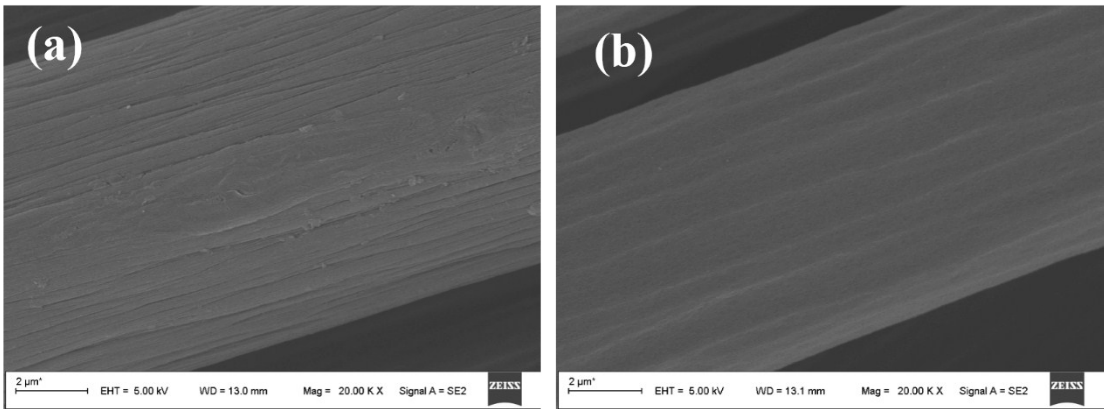

Fig. S2. SEM image of (a) Untreated Carbon Cloth, (b) Electro-etched of Carbon Cloth.

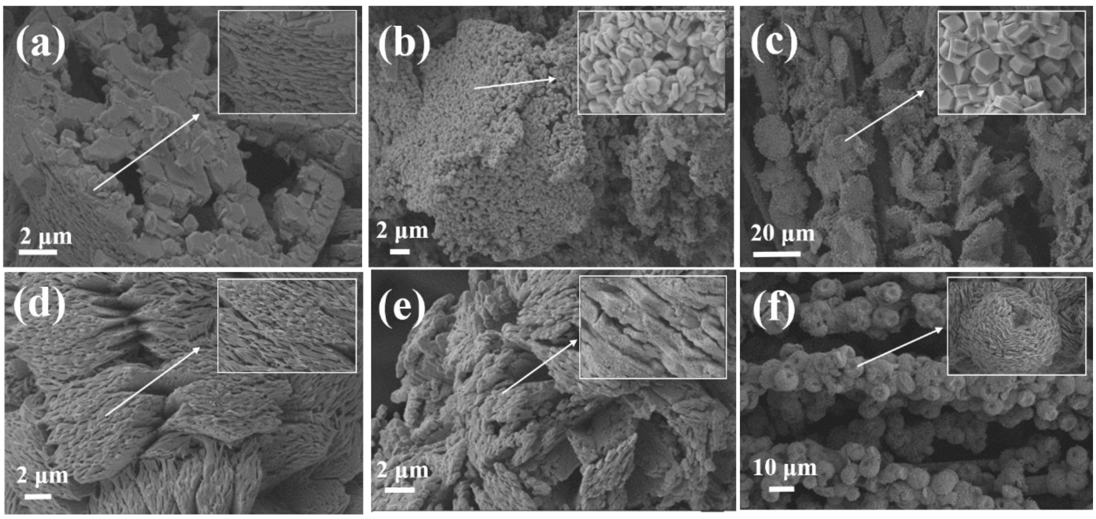

Fig. S3. SEM image of (a)CoP_2/CC -1, (b)CoP_2/CC -2, (c)CoP_2/CC -3, (d)CoP_2/CC -4, (e) CoP_2/CC -5 and (f)CoP_2/CC -0.

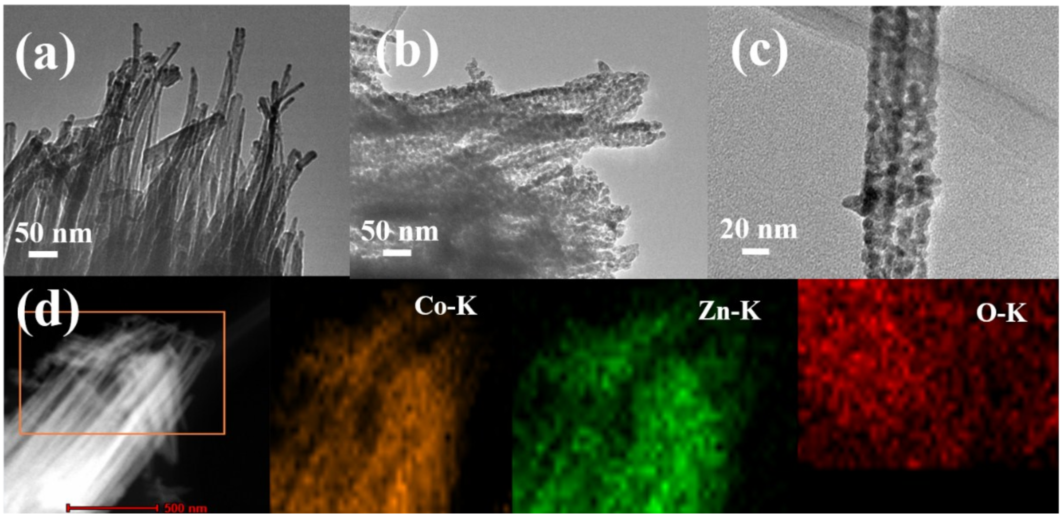

Fig. S4. (a) TEM image of $Co_xZn_{1-x}OHF$; (b, c) TEM image of Co_2O_3@ZnO; (d) Element mapping of the Co_2O_3@ZnO.

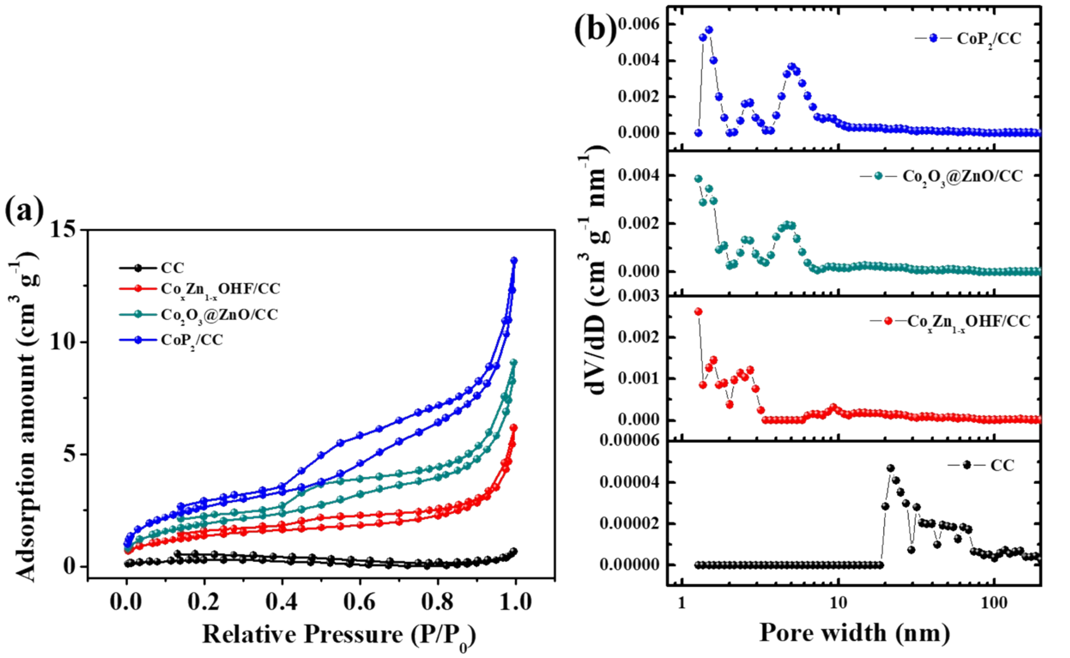

Fig. S5. (a) Nitrogen adsorption-desorption isotherm and (b) pore size distribution plot of CC, $Co_xZn_{1-x}OHF$/CC, Co_2O_3@ZnO/CC and CoP_2/CC samples.

The porous structure of the samples is further determined by a N_2 adsorption−desorption test. As shown in Fig. S5(a), the typical type-IV isotherm with a distinct hysteresis loop was observed for CoP_2/CC catalyst, indicating abundant mesoporous structure.[18] The BET surface area of CC, Co_xZn_{1-x}OHF/CC, Co_2O_3@ZnO/CC and CoP_2/CC are 0.9252, 4.8070, 6.8028 and 9.5234 m^2 g^{-1}. Obviously, an increase of BET surface area from 6.8028 m^2 g^{-1} (Co_2O_3@ZnO/CC) to 9.5234 m^2 g^{-1} (CoP_2/CC) was observed, indicating that the alkaline etching of Co_2O_3@ZnO/CC to remove the ZnO matrix obviously increases the surface area of CoP_2/CC. Moreover, the hierarchical porous configuration of the samples is also confirmed by the pore size distribution plot, as shown in Fig. S5(b). The meso/macropores of CC was obvised. The micropores of Co_xZn_{1-x}OHF/CC, Co_2O_3@ZnO/CC and CoP_2/CC are centered at around 1.27, 1.27, and 1.48 nm, respectively. The two region mesopores of Co_xZn_{1-x}OHF/CC, Co_2O_3@ZnO/CC and CoP_2/CC are centered at around 2.52 and 2.73, 2.73 and 4.66, 2.73 and 5.04 nm, respectively. It is obviously observed that CoP_2/CC shows a relatively abundant micropores. This result is consistent with TEM image of Fig.2 and Fig.S4. The porosity of CoP_2/CC catalyst is beneficial for mass transport for electrocatalysis.[19]

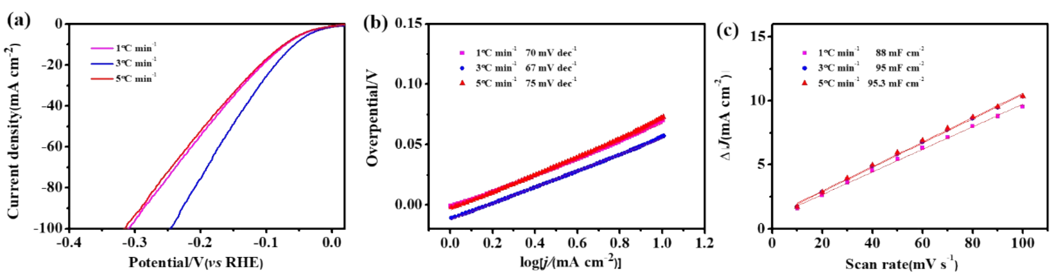

Fig. S6. (a)LSV curves, (b) Tafel plots, and (c) ECSA of CoP_2/CC-4 at different anneling rate in 0.5M H_2SO_4 solution.

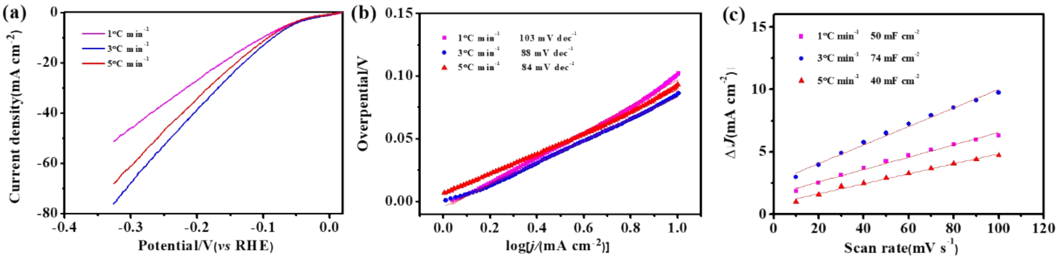

Fig. S7. (a)LSV curves, (b) Tafel plots, and (c) ECSA of CoP_2/CC-4 at different anneling rate in 1M KOH solution.

Table S1. Comparison of HER performance in acidic electrolytes for CoP_2/CC-4 with other HER electrocatalysts.

Catalysts	η_j (mV)	j (mA cm^{-2})	Tafel slope (mV dec^{-1})	exchange current density (mA cm^{-2})	Loading mass (mg cm^{-2})	Ref.
Co_2P@C/CC	103	10	40.8	0.29	-	1
MoP/RGO	118	20	58	0.201	-	2
CoS/CC	212	10	112	-	3.5	3
CoP-NTs	152	10	50	-	0.35	4
MoS_2/G-20	110	10	67.4	0.14	-	5
Mo_2C nanotube	172 197	10 20	62	0.017	-	6
CoP_3 CPs	78	10	53	0.209	-	7
Co/CoP-5	178 195	10 20	59.1	-	0.88	8
HNDCM-Co/CoP	135	10	64	-	-	9
Ni_2P–CoP	105	10	64	-	-	10
Co_2P/Ti	95 109	10 20		-	1	11
CoP@NC	78	10	49	-	0.306	12
CoP/CC	67 100	10 20	51	0.288	0.92	13
mp-Ni_2P/Ni foam	140	20	68.9	-	2	14
CoP_2/CC-4	56 86	10 20	67	1.5348	4.69	This work

Table S2. Comparison of HER performance in alkaline electrolytes for CoP_2/CC-4 with other HER electrocatalysts.

Catalysts	η_j (mV)	j (mA cm^{-2})	Tafel slope (mVdec^{-1})	exchange current density (mA cm^{-2})	Loading mass (mg cm^{-2})	Ref.
Co-B@CoO/Ti	61	10	78	-	4.87	15
Fe-Doped CoP	78	10	75	-	1.03	16
CoS/CC	197	10	105	-	3.5	3
f-CoP/CoP_2/Al_2O_3	300	10	73	-	0.2	17
Co/CoP-5	253	10	73.8	-	0.88	8
HNDCM-Co/CoP	135	10	64	-	-	9
Co_2P/Ti	95 109	10 20		-	1	11
CoP@NC	129	10	58	-	0.306	12
CoP/CC	209	10	129	0.288	0.92	13
mp-Ni_2P/Ni foam	140	20	68.9	-	2	14
CoP_2/CC-4	72 114	10 20	88	1.1236	4.69	This work

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