Supporting Information

Ethylene-Glycol Ligand Environment Facilitates Highly Efficient Hydrogen Evolution of Pt/CoP through Proton Concentrating and Hydrogen Spillover

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# J. Li and H. Liu contributed equally to this work.

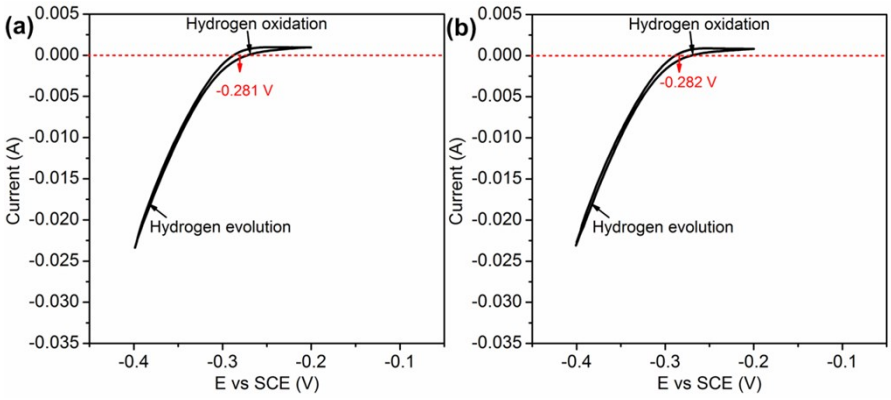

Fig. S1 (a) The CV result of RHE calibration in 0.5 M H_2SO_4 before durability test, E(RHE) = E(SCE) + 0.281 V. (b) The CV result of RHE calibration in 0.5 M H_2SO_4 after durability test, E(RHE) = E(SCE) + 0.282 V.

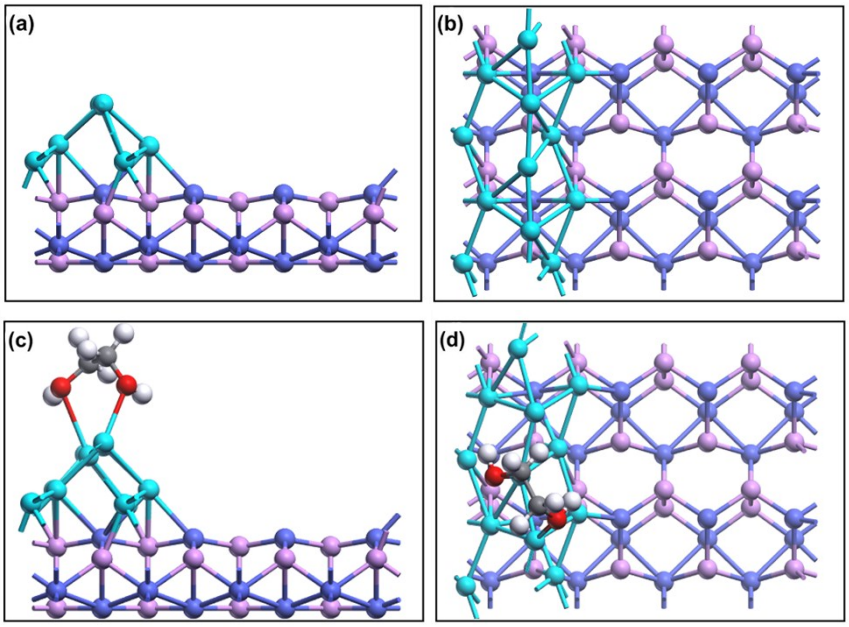

Fig. S2 The optimized Pt/CoP and EG-Pt/CoP geomertries for DFT calculation. Structure of Pt/CoP was showed in (a) side view and (b) top view; Structure of EG-Pt/CoP was showed in (c) side view and (d) top view.

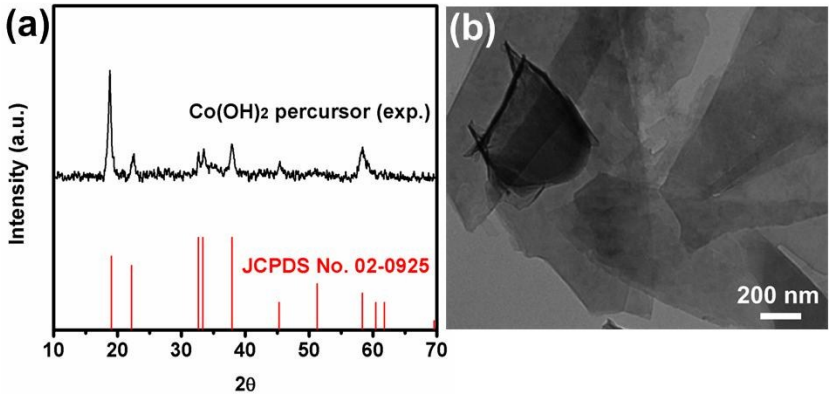

Fig. S3 (a) XRD pattern and (b) TEM image of as-prepared $Co(OH)_2$ precursor.

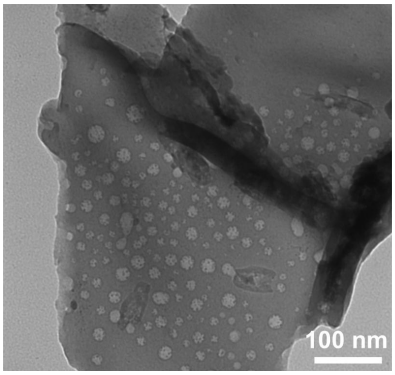

Fig. S4. TEM image of as-synthesized CoP catalysts.

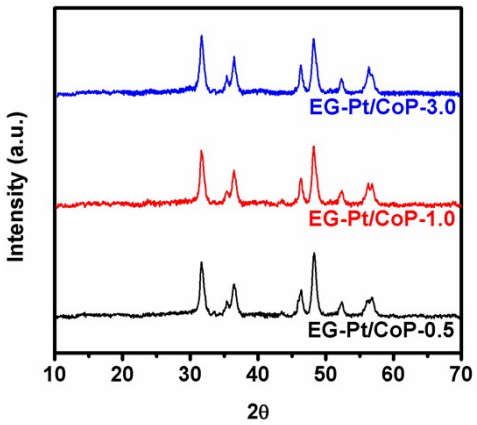

Fig. S5 XRD patterns of the EG-Pt/CoP-0.5, EG-Pt/CoP-1.0 and EG-Pt/CoP-3.0 hybrid catalysts.

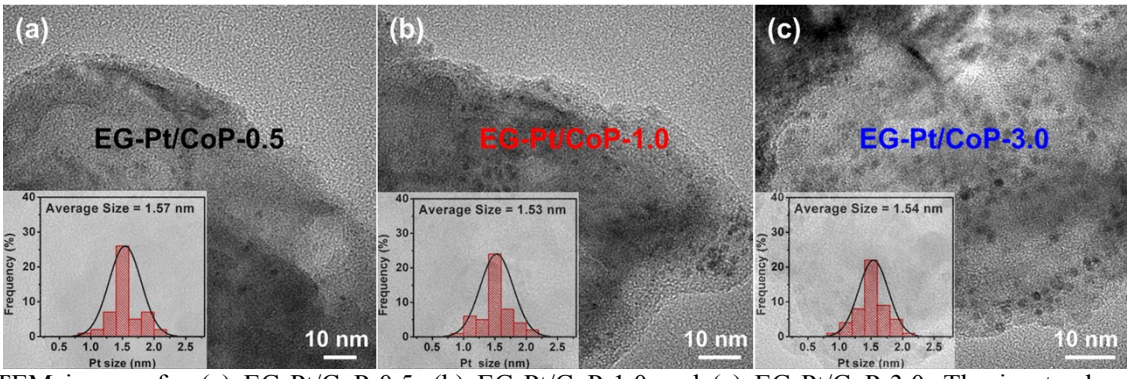

Fig. S6 TEM images for (a) EG-Pt/CoP-0.5, (b) EG-Pt/CoP-1.0 and (c) EG-Pt/CoP-3.0. The insets show the size distributions of the loaded Pt nanoparticles.

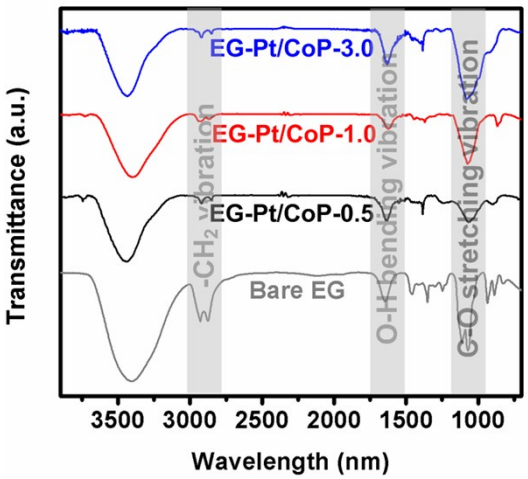

Fig. S7 Infrared transmission spectra for EG, EG-Pt/CoP-0.5, EG-Pt/CoP-1.0 and EG-Pt/CoP-3.0.

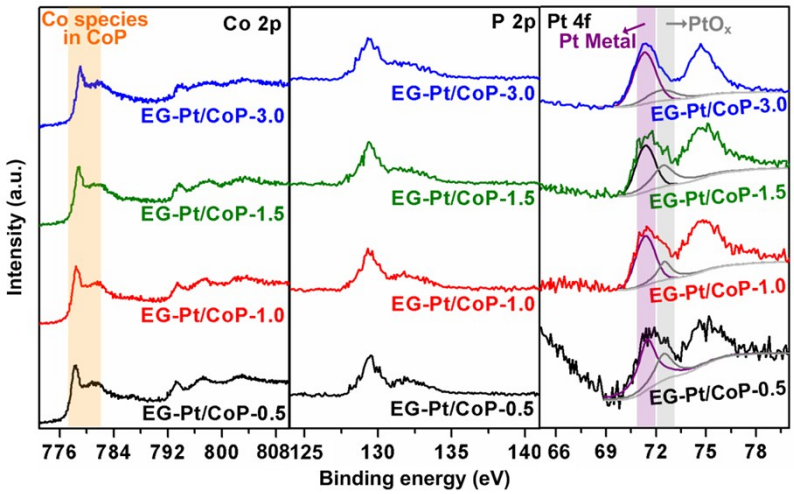

Fig. S8 High-resolution XPS spectra in Co 2p, P 2p and Pt 4f region for EG-Pt/CoP catalysts.

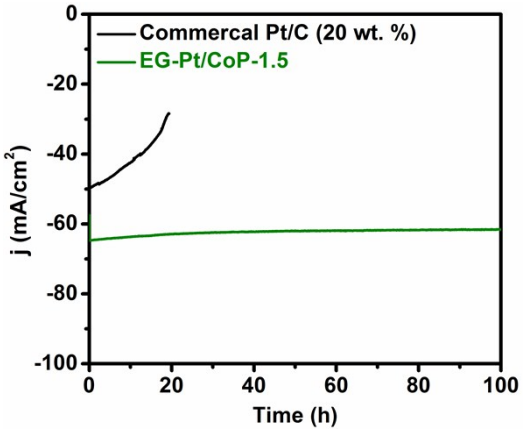

Fig. S9 Time-dependent HER durability of the EG-Pt/CoP-1.5 and commercial Pt/C (20 wt. %) catalysts under an overpotential of -100 mV in 0.5 M H_2SO_4.

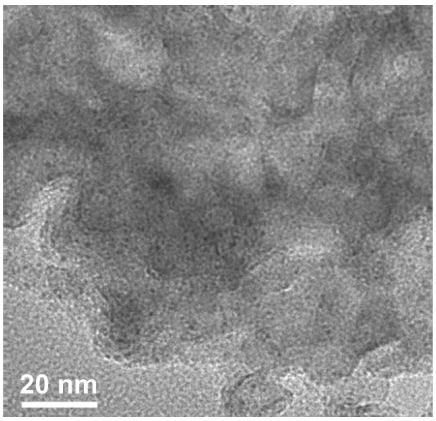

Fig. S10 TEM images of the EG-Pt/CoP-1.5 catalysts after 100 h HER in 0.5 M H_2SO_4.

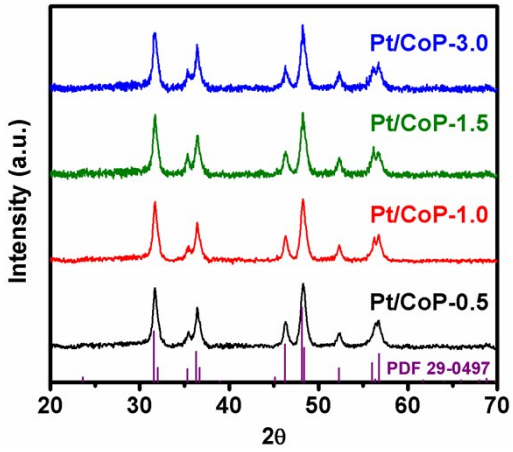

Fig. S11 XRD patterns of the Pt/CoP-0.5, Pt/CoP-1.0, Pt/CoP-1.5 and Pt/CoP-3.0 hybrid catalysts.

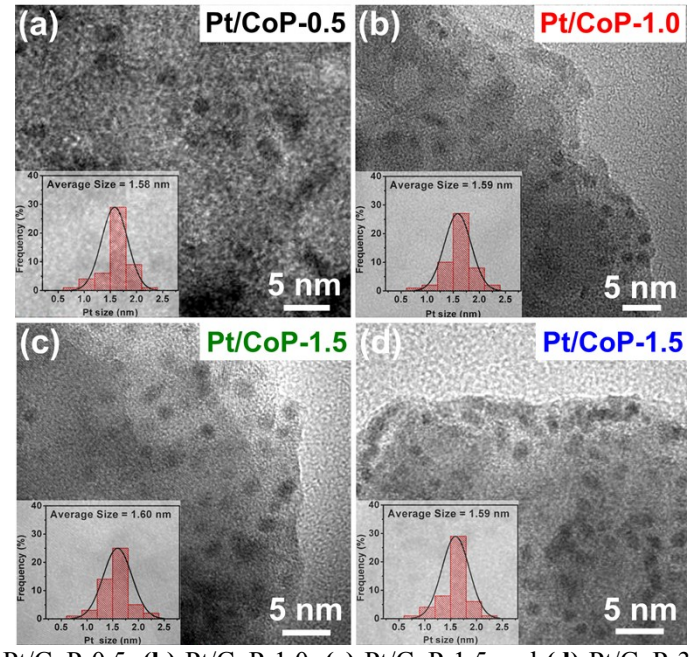

Fig. S12 TEM images of **(a)** Pt/CoP-0.5, **(b)** Pt/CoP-1.0, **(c)** Pt/CoP-1.5 and **(d)** Pt/CoP-3.0. The insets show the size distributions of loaded Pt nanoparticles.

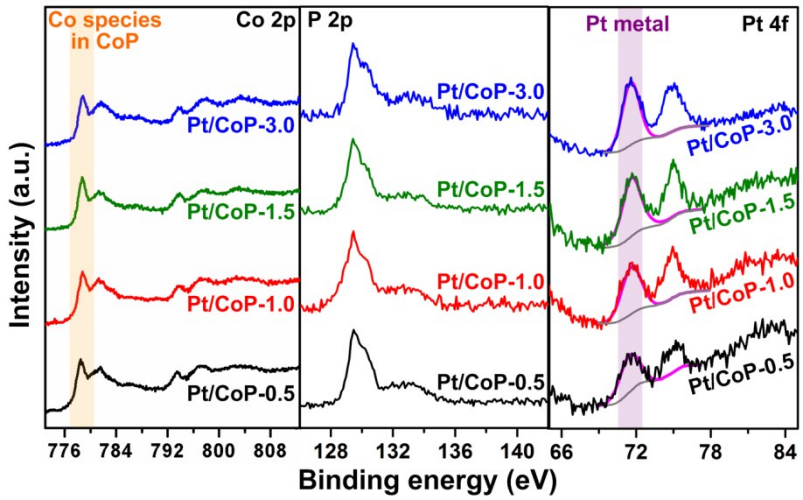

Fig. S13 High-resolution XPS spectra in Co 2p, P 2p and Pt 4f region for Pt/CoP catalysts.

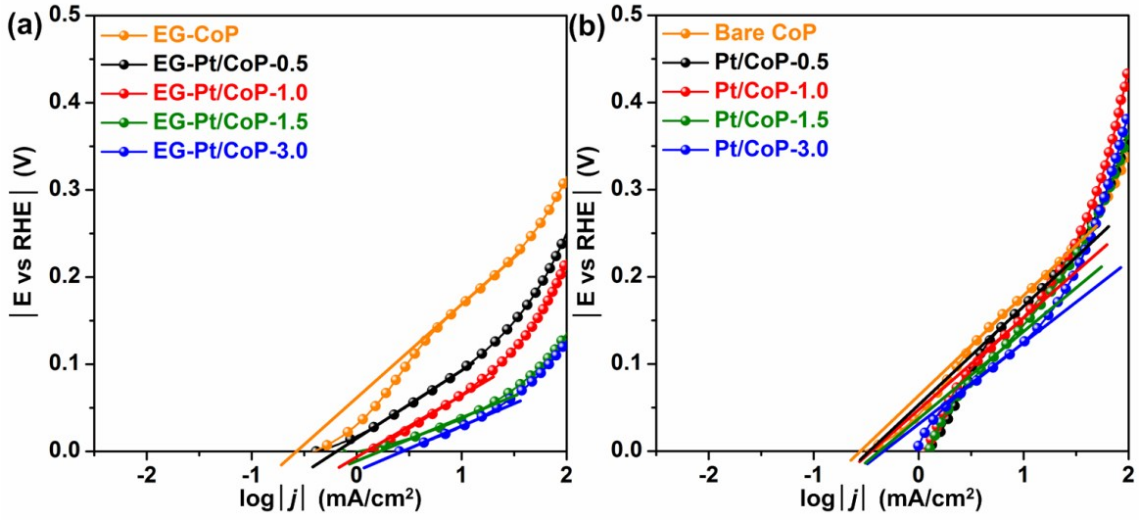

Fig. S14 Exchange current density of various EG-Pt/CoP catalysts for HER.

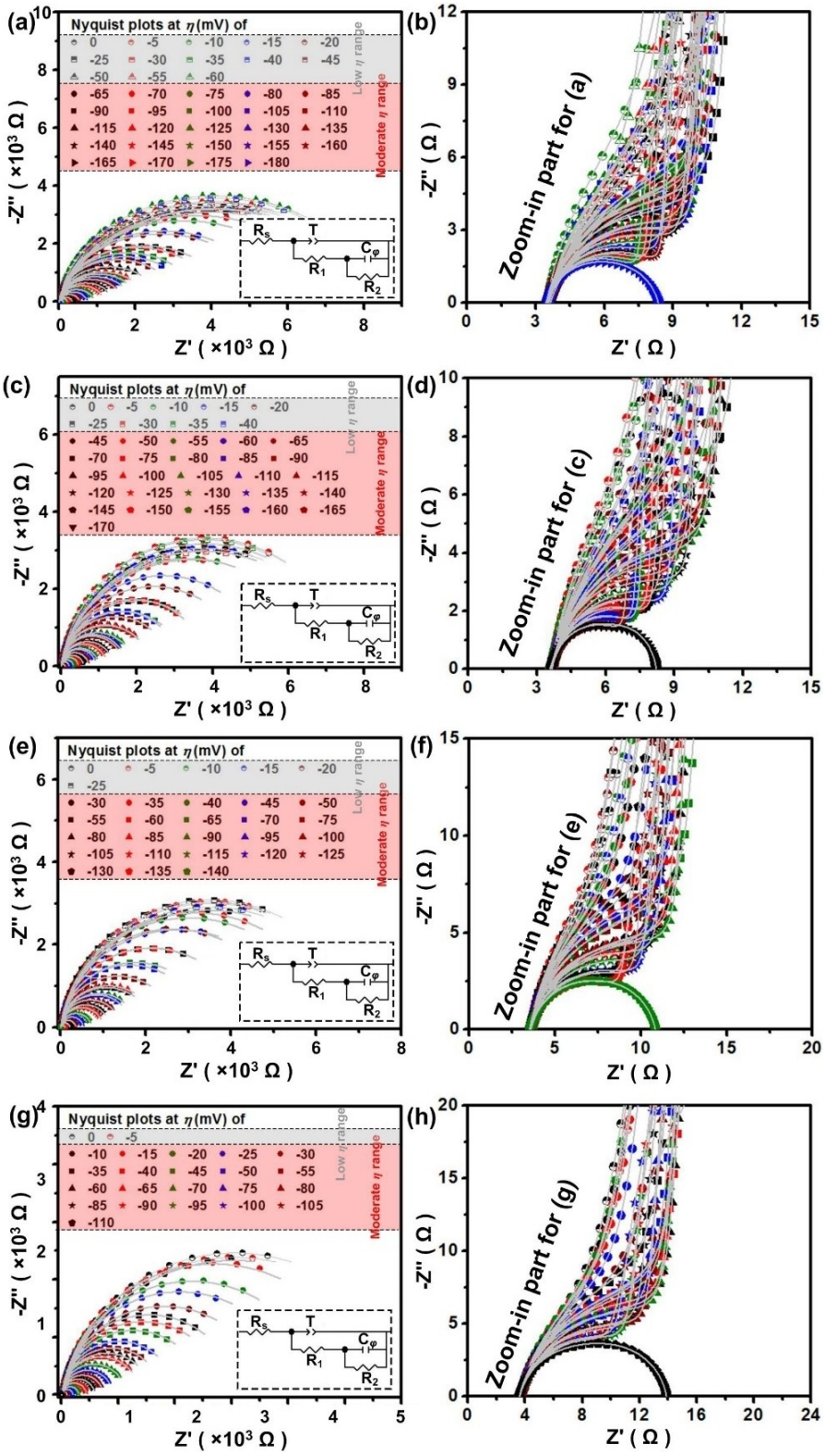

Fig. S15 Nyquist plots for **(a)** Pt/CoP-0.5, **(c)** Pt/CoP-1.0, **(e)** Pt/CoP-1.5 and **(g)** Pt/CoP-3.0 catalysts in 0.5 M H_2SO_4 at various HER overpotentials. Zoom-in parts were correspondingly presented in **(b), (d), (f)** and **(h)**. The scattered symbols represent the experimental results and the solid lines are simulation fitted results. The inset at the bottom right shows the equivalent circuit for the simulation. The fitted parameters are summarized in Table S3. The gray and red areas are identified as low and moderate overpotential range based on such fitted parameters.

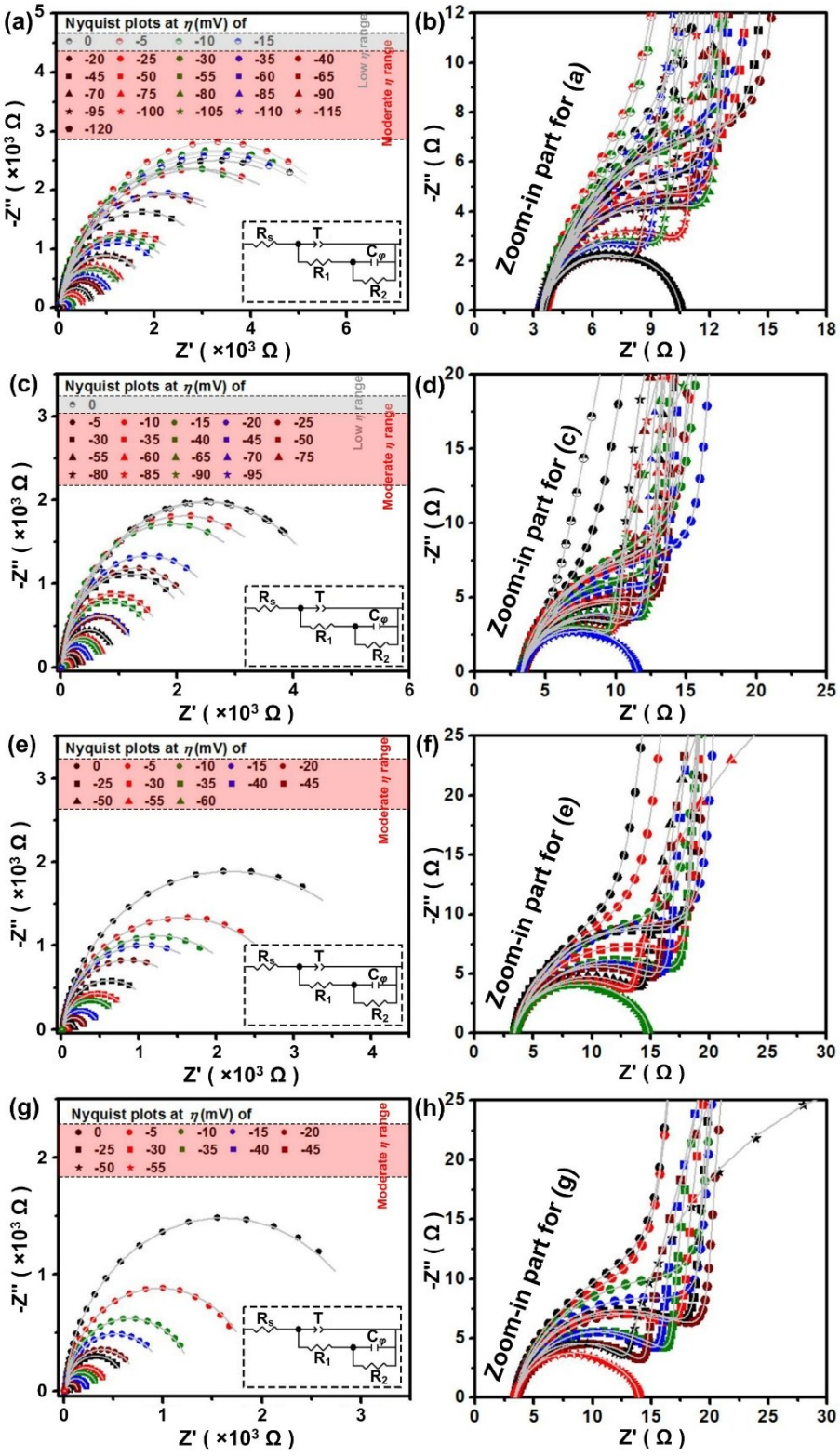

Fig. S16 Nyquist plots of **(a)** EG-Pt/CoP-0.5, **(c)** EG-Pt/CoP-1.0, **(e)** EG-Pt/CoP-1.5 and **(g)** EG-Pt/CoP-3.0 catalysts in 0.5 M H_2SO_4 at various HER overpotentials. Zoom-in parts were correspondingly presented in **(b), (d), (f)** and **(h)**. The scattered symbols represent the experimental results and the solid lines are simulation fitted results. The inset at the bottom right shows the equivalent circuit for the simulation. The fitted parameters are summarized in Table S4. The gray and red areas are identified as low and moderate overpotential range based on such fitted parameters.

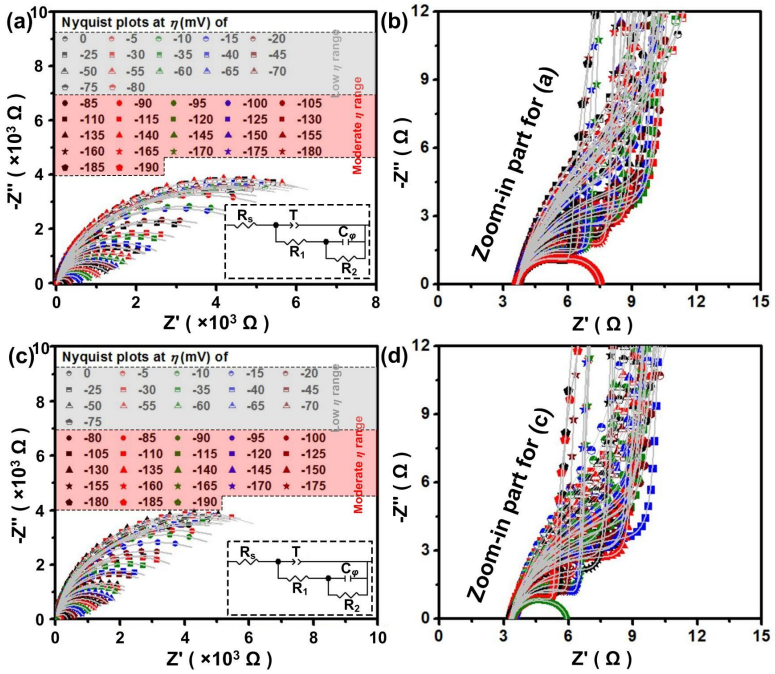

Fig. S17 Nyquist plots of **(a)** CoP **(b)** EG-CoP references in 0.5 M H_2SO_4 at various HER overpotentials. The scattered symbols represent the experimental results and the solid lines are simulation fitted results. The inset at the bottom right shows the equivalent circuit for the simulation. The fitted parameters are summarized in Table S3 and S4. The gray and red areas are identified as low and moderate overpotential range based on such fitted parameters.

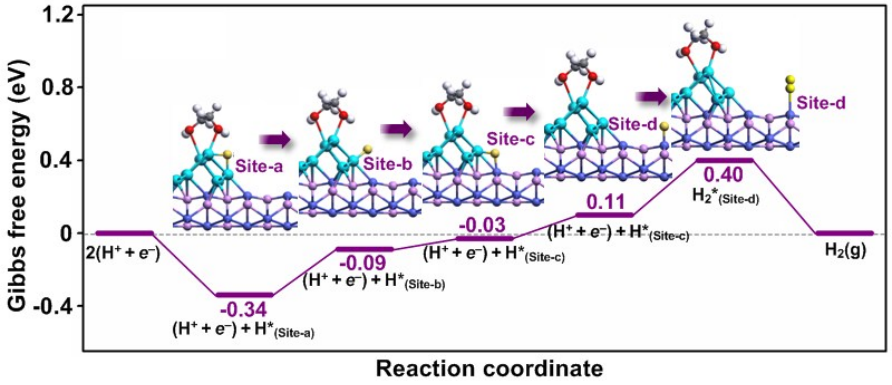

Fig. S18 Calculated free energy diagram for HER process on EG-Pt/CoP.

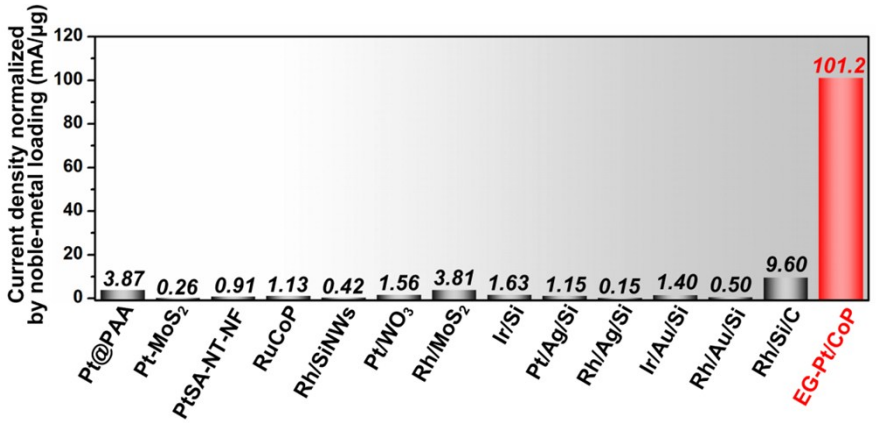

Fig. S19 Comparison of noble-metal utilization activity for EG-Pt/CoP-1.5 with the state-of-the-art noble-metal based and hydrogen spillover electrocatalysts at 0.1 V vs RHE in acid media.

Table S1. The actual Pt loadings of as-prepared EG-Pt/CoP and Pt/CoP catalysts.

Sample	EG-Pt/CoP				Pt/CoP			
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
Calculated Pt loading (wt. %)	0.5	1.0	1.5	3.0	0.5	1.0	1.5	3.0
Actual Pt loading (wt. %)	0.45	0.98	1.45	2.93	0.46	0.99	1.47	2.94

Table S2. Comparison of HER performance in acidic media for EG-Pt/CoP-1.5 with the state-of-the-art HER catalysts.

Catalyst	η_{10} [mV]	η_{100} [mV]	j_0 [mA/cm^2]	Tafel slope [mV/dec]	Catalyst loading [mg/cm^2]	Noble metal loading [mg/cm^2]	Duability [h]	Ref
EG-Pt/CoP-1.5	21	108	1.67	42.5	0.102	0.001	100	This work
$Pt_{tripods}$@PAA	+5	30	—	26	0.079	0.079	1.67	Ref. 1
Pt-MoS_2	143	—	—	96	—	0.018	—	Ref. 2
ALD50Pt/NG	42	—	—	29	—	0.0011	—	Ref. 3
Pt/MoS_2	34	—	—	25	0.07	0.0073	35	Ref. 4
PtSA-NT-NF	30	88	—	—	—	0.14	—	Ref. 5
RuCoP	11	77	—	31	0.3	0.06	150	Ref. 6
Ru_2P@NPS	38	—	1.99	38	1.0	0.233	10	Ref. 7
Ru/C_3N_4	68	—	—	—	0.204	0.041	—	Ref. 8
Ni_2P NPs	116	—	0.033	46	1.0	0	—	Ref. 9
CoP NWs	67	204	0.288	51	0.92	0	22	Ref. 10
Co-Fe-P 3D electrode	66	—	0.5	45	1.0	0	—	Ref. 11
Mo-W-P	83	138	0.288	52	4.0	0	8	Ref. 12
Co-Ni-S-P/ graphene	77	140	—	48	3.0	0	—	Ref. 13
PANI/CoP	57	122	—	34.5	0.8	0	30	Ref. 14
$Ni_{0.33}Ce_{0.67}Se_2$/ CFP	67	—	0.184	35	—	0	40	Ref. 15
$Ni_{0.33}Co_{0.67}S_2$ NWs	73	118	—	44.1	0.3	0	< 3	Ref. 16
WO_2-Carbon mesoporous nanowires	58	—	0.64	46	0.35	0	10	Ref. 17

Table S3. The fitted parameters of the EIS data of various Pt/CoP catalysts as well as CoP reference for HER.

Catalysts	η (mV)	R_s (Ω)	T (F s^{n-1})	R_1 (Ω)	n_1	R_2 (Ω)	C_φ (F)
CoP	0	3.64	0.0040	25.4	0.81	8805	0.0017
	-5	3.61	0.0044	24.4	0.83	8802	0.0026
	-10	3.66	0.0046	24.0	0.8	8798	0.0025
	-15	3.62	0.0045	23.1	0.83	8795	0.0025
	-20	3.59	0.0044	22.8	0.86	8791	0.0024
	-25	3.66	0.0045	21.4	0.88	8788	0.0026
	-30	3.64	0.0039	20.9	0.81	8785	0.0038
	-35	36.5	0.0037	20.0	0.83	8781	0.0032
	-40	3.61	0.0041	19.1	0.85	8779	0.0040
	-45	3.62	0.0043	17.9	0.82	8777	0.0030
	-50	3.60	0.0044	17.2	0.8	8774	0.0043
	-55	3.67	0.0039	16.9	0.88	8770	0.0033
	-60	3.65	0.0041	16.1	0.81	8765	0.0042
	-65	3.61	0.0047	15.2	0.83	8762	0.0031
	-70	3.63	0.0044	14.1	0.85	8757	0.0042
	-75	3.64	0.0042	13.6	0.87	8755	0.0041
	-80	3.7	0.0041	13.0	0.87	8750	0.0049
	-85	3.67	0.0042	12.5	0.83	8000	0.00494
	-90	3.64	0.0045	12.1	0.88	7252	0.0057
	-95	3.66	0.0044	11.9	0.85	6494	0.0071
	-100	3.62	0.0042	11.4	0.86	6144	0.0082
	-105	3.63	0.0041	10.4	0.81	5446	0.0104
	-110	3.64	0.0044	9.7	0.85	4941	0.0123
	-115	3.67	0.004	9.2	0.82	4206	0.0143
	-120	3.61	0.0039	8.6	0.8	3921	0.0152
	-125	3.66	0.0037	8.2	0.86	3160	0.0176
	-130	3.62	0.0041	7.6	0.83	2896	0.0195
	-135	3.66	0.0044	7.1	0.86	2813	0.0203
	-140	3.64	0.0039	6.7	0.83	2446	0.0217
	-145	3.61	0.0042	6.5	0.85	2103	0.0224

	-150	3.65	0.0045	6.1	0.88	1780	0.0238
	-155	3.64	0.0044	5.8	0.82	1682	0.024
	-160	3.67	0.004	5.3	0.83	1432	0.0246
	-165	3.68	0.0036	5.0	0.8	1155	0.026
	-170	3.63	0.004	4.2	0.81	880	0.0265
	-175	3.64	0.0042	3.9	0.82	616	0.0267
	-180	3.66	0.0045	3.5	0.83	358	0.0275
	-185	3.63	0.0042	3.0	0.81	162	0.0285
	-190	3.61	0.0046	2.9	0.83	—	—
	0	3.51	0.0039	26.2	0.83	8218	0.0006
	-5	3.54	0.004	25.4	0.81	8214	0.0026
	-10	3.49	0.0041	24.1	0.9	8211	0.0025
	-15	3.56	0.0038	23.5	0.81	8206	0.0020
	-20	3.53	0.0042	22.1	0.85	8202	0.0018
	-25	3.57	0.0044	21.0	0.83	8199	0.0020
	-30	3.51	0.004	20.7	0.8	8194	0.0022
	-35	3.51	0.0045	19.8	0.85	8192	0.0016
Pt/CoP-0.5	-40	3.54	0.0037	19.0	0.88	8190	0.0019
	-45	3.53	0.0038	18.1	0.8	8186	0.003
	-50	3.50	0.0044	17.0	0.81	8181	0.0016
	-55	3.53	0.0046	16.4	0.86	8177	0.0016
	-60	3.57	0.0042	15.2	0.9	8170	0.0025
	-65	3.64	0.004	14.7	0.78	8166	0.0026
	-70	3.50	0.0039	14.0	0.81	7330	0.0042
	-75	3.52	0.0037	13.1	0.82	6612	0.0063
	-80	3.49	0.0041	12.5	0.85	5521	0.0077
	-85	3.51	0.0037	11.9	0.82	5415	0.0082
	-90	3.57	0.0034	11.4	0.8	4504	0.0084
	-95	3.55	0.0039	10.7	0.85	4135	0.011
	-100	3.53	0.0042	10.3	0.87	3652	0.0115
	-105	3.47	0.0038	10.0	0.82	3459	0.0137
	-110	3.46	0.0041	9.4	0.88	3079	0.0162

	-115	3.47	0.0044	8.9	0.85	2622	0.0176
	-120	3.50	0.0045	8.6	0.8	2307	0.018
	-125	3.51	0.0039	8.5	0.82	2073	0.021
	-130	3.53	0.0037	8.1	0.81	1882	0.0212
	-135	3.49	0.0036	7.7	0.83	1662	0.0226
	-140	3.54	0.004	7.4	0.81	1404	0.0256
	-145	3.51	0.0042	7.0	0.83	1179	0.0263
	-150	3.47	0.0049	6.6	0.8	915	0.0283
	-155	3.46	0.0039	6.1	0.81	726	0.0296
	-160	3.53	0.0033	5.8	0.79	529	0.030
	-165	3.44	0.0039	5.5	0.8	340	0.032
	-170	3.47	0.0037	5.1	0.81	206	0.033
	-175	3.47	0.0035	4.7	0.83	98	0.0332
	-180	3.46	0.0038	4.4	0.82	—	—
	0	3.61	0.0044	25.9	0.88	7632	0.0011
	-5	3.62	0.0047	24.7	0.89	7625	0.0016
	-10	3.57	0.005	24.0	0.86	7619	0.002
	-15	3.59	0.0049	23.1	0.83	7614	0.0023
	-20	3.60	0.0046	22.2	0.85	7611	0.0025
	-25	3.64	0.0043	21.8	0.83	7606	0.0021
Pt/CoP-1.0	-30	3.63	0.0047	21.0	0.81	7600	0.0028
	-35	3.61	0.0051	20.4	0.88	7591	0.0024
	-40	3.60	0.0049	19.4	0.83	7583	0.0021
	-45	3.62	0.0041	18.6	0.81	7583	0.0025
	-50	3.61	0.0052	18.0	0.81	6941	0.0040
	-55	3.57	0.0047	17.7	0.83	6761	0.0040
	-60	3.64	0.0045	16.1	0.85	5452	0.0051
	-65	3.60	0.0044	15.3	0.82	4910	0.0060
	-70	3.63	0.0043	14.9	0.8	4083	0.0070
	-75	3.62	0.0047	14.1	0.87	3845	0.0079
	-80	3.63	0.005	13.0	0.82	3299	0.010
	-85	3.61	0.0052	12.2	0.86	3149	0.011

	-90	3.66	0.0047	11.7	0.82	2908	0.012
	-95	3.62	0.0043	10.8	0.8	2395	0.013
	-100	3.60	0.0044	10.3	0.83	2345	0.0145
	-105	3.63	0.0047	10.0	0.81	1928	0.017
	-110	3.65	0.0049	8.9	0.88	1712	0.019
	-115	3.66	0.0044	8.3	0.87	1635	0.021
	-120	3.62	0.0042	7.9	0.81	1378	0.022
	-125	3.63	0.0046	7.6	0.86	1208	0.023
	-130	3.60	0.0045	7.1	0.8	1001	0.025
	-135	3.59	0.004	6.4	0.8	926	0.0271
	-140	3.61	0.0047	6.1	0.83	729	0.0285
	-145	3.64	0.0044	5.5	0.81	594	0.030
	-150	3.62	0.004	5.2	0.86	448	0.0313
	-155	3.57	0.0046	4.7	0.82	318	0.0335
	-160	3.62	0.0044	4.4	0.87	206	0.0345
	-165	3.60	0.0049	3.9	0.83	99	0.036
	-170	3.61	0.005	3.6	0.86	—	—
	0	3.55	0.006	25.4	0.87	7054	0.0017
	-5	3.53	0.0061	25.0	0.88	7050	0.0027
	-10	3.49	0.0057	24.4	0.85	7041	0.0025
	-15	3.56	0.0055	23.1	0.85	7032	0.0012
Pt/CoP-1.5	-20	3.58	0.0063	22.2	0.88	7020	0.0019
	-25	3.51	0.0054	21.0	0.89	7011	0.0021
	-30	3.57	0.0055	20.4	0.83	7000	0.0034
	-35	3.55	0.005	19.3	0.87	6376	0.0041
	-40	3.58	0.006	18.9	0.88	6027	0.0049
	-45	3.59	0.0061	17.4	0.85	5523	0.0064
	-50	3.53	0.0054	17.1	0.88	5262	0.0084
	-55	3.51	0.0055	16.6	0.87	4243	0.0103
	-60	3.56	0.0058	15.7	0.86	4234	0.0132
	-65	3.53	0.0055	14.9	0.83	3522	0.0155
	-70	3.51	0.006	13.9	0.88	3246	0.0167

	-75	3.53	0.0061	12.8	0.87	2674	0.018
	-80	3.55	0.0054	12.3	0.8	2169	0.021
	-85	3.56	0.0058	11.9	0.81	2246	0.022
	-90	3.58	0.0052	11.6	0.8	1804	0.024
	-95	3.51	0.0055	10.6	0.85	1669	0.026
	-100	3.54	0.006	10.2	0.87	1396	0.028
	-105	3.55	0.0053	9.9	0.83	1157	0.030
	-110	3.57	0.0051	9.1	0.88	983	0.031
	-115	3.58	0.0055	8.9	0.83	712	0.0323
	-120	3.55	0.005	8.3	0.79	527	0.034
	-125	3.58	0.0052	7.7	0.81	348	0.035
	-130	3.52	0.0057	7.1	0.85	212	0.0374
	-135	3.53	0.005	6.6	0.81	95	0.0382
	-140	3.54	0.0051	6.3	0.83	—	—
Pt/CoP-3.0	0	3.61	0.0061	26.1	0.83	6131	0.0035
	-5	3.57	0.0062	25.2	0.81	6115	0.0033
	-10	3.60	0.007	24.1	0.8	6100	0.0038
	-15	3.62	0.006	23.6	0.85	5389	0.0050
	-20	3.59	0.0064	22.4	0.86	4596	0.0051
	-25	3.63	0.0071	21.0	0.85	4179	0.0079
	-30	3.61	0.0064	20.2	0.83	3634	0.0088
	-35	3.62	0.0059	19.6	0.86	3094	0.012
	-40	3.61	0.0058	18.7	0.83	2879	0.0148
	-45	3.65	0.0062	17.7	0.83	2523	0.0171
	-50	3.61	0.0068	17.0	0.86	2019	0.0212
	-55	3.67	0.0069	16.3	0.85	1770	0.0244
	-60	3.64	0.0063	15.1	0.82	1590	0.0283
	-65	3.61	0.0058	14.6	0.88	1378	0.0306
	-70	3.59	0.0056	13.9	0.86	1122	0.033
	-75	3.63	0.0066	13.0	0.88	891	0.0348
	-80	3.61	0.006	12.2	0.83	729	0.0362
	-85	3.63	0.0065	11.6	0.86	575	0.0382

	-90	3.62	0.0066	10.7	0.87	428	0.0393
	-95	3.61	0.0065	10.1	0.83	293	0.040
	-100	3.62	0.0068	9.4	0.88	191	0.0415
	-105	3.63	0.007	8.8	0.89	89	0.0433
	-110	3.59	0.0066	8.3	0.86	—	—

Table S4. The fitted parameters of the EIS data of various EG-Pt/CoP catalysts as well as EG-CoP reference for HER.

Catalysts	η (mV)	R_s (Ω)	T (F s^{n-1})	R_1 (Ω)	n_1	R_2 (Ω)	C_φ (F)
EG-CoP	0	3.41	0.0047	23.8	0.83	8781	0.0017
	-5	3.43	0.005	22.6	0.81	8777	0.0026
	-10	3.44	0.0051	22.0	0.86	8774	0.0024
	-15	3.40	0.0053	21.1	0.88	8770	0.0034
	-20	3.45	0.0044	20.0	0.82	8763	0.0030
	-25	3.39	0.0049	19.3	0.85	8757	0.0032
	-30	3.38	0.0041	18.5	0.88	8752	0.0049
	-35	3.42	0.0046	17.0	0.83	8747	0.0035
	-40	3.44	0.0047	16.7	0.82	8745	0.0038
	-45	3.44	0.0051	16.3	0.81	8737	0.0030
	-50	3.46	0.0047	15.2	0.89	8730	0.0037
	-55	3.47	0.0046	14.9	0.87	8725	0.0033
	-60	3.43	0.0044	14.0	0.8	8721	0.0044
	-65	3.44	0.005	13.3	0.81	8720	0.0030
	-70	3.40	0.0051	13.0	0.82	8713	0.0040
	-75	3.42	0.0047	12.5	0.86	8706	0.0041
	-80	3.29	0.0039	12.1	0.79	8700	0.0052
	-85	3.31	0.0038	11.8	0.83	7601	0.0064
	-90	3.34	0.0041	11.4	0.88	6799	0.0077
	-95	3.38	0.0044	11.0	0.86	6321	0.0083

	-100	3.33	0.0045	10.8	0.83	5721	0.0102
	-105	3.29	0.0051	9.9	0.8	5575	0.0107
	-110	3.27	0.0041	9.5	0.89	4876	0.0126
	-115	3.39	0.0045	9.2	0.86	4457	0.0143
	-120	3.44	0.0039	8.8	0.81	3991	0.0158
	-125	3.31	0.0049	8.5	0.83	3692	0.0162
	-130	3.30	0.005	7.6	0.8	3028	0.0189
	-135	3.25	0.004	7.2	0.79	2828	0.0192
	-140	3.35	0.006	7.1	0.9	2493	0.0203
	-145	3.37	0.004	7.0	0.88	2113	0.0212
	-150	3.38	0.0045	6.0	0.89	1850	0.0236
	-155	3.40	0.005	5.5	0.81	1650	0.0250
	-160	3.41	0.0052	4.3	0.86	1389	0.0253
	-165	3.34	0.0039	4.0	0.81	1120	0.0264
	-170	3.39	0.0033	3.6	0.79	892	0.0270
	-175	3.40	0.0036	3.1	0.85	608	0.0281
	-180	3.29	0.0041	2.8	0.87	367	0.0286
	-185	3.40	0.0044	2.3	0.83	164	0.029
	-190	3.42	0.0043	2.1	0.82	—	—
	0	3.49	0.0034	24.9	0.81	6666	0.0023
	-5	3.46	0.0044	23.5	0.86	6647	0.0026
	-10	3.44	0.0045	22.1	0.83	6635	0.0024
	-15	3.47	0.0039	21.0	0.8	6622	0.0027
	-20	3.52	0.0044	20.6	0.78	6600	0.0033
	-25	3.47	0.0039	19.8	0.79	5923	0.0046
EG-Pt/CoP - 0.5	-30	3.51	0.0045	19.0	0.85	5360	0.0084
	-35	3.43	0.0049	18.1	0.82	4477	0.012
	-40	3.52	0.0038	17.4	0.83	4249	0.0137
	-45	3.49	0.0041	16.0	0.88	3453	0.0182
	-50	3.59	0.0049	15.2	0.82	2877	0.0169
	-55	3.43	0.0051	13.9	0.92	2527	0.021
	-60	3.41	0.0044	13.0	0.86	2379	0.0211

	-65	3.38	0.005	12.6	0.79	1998	0.0233
	-70	3.41	0.0054	12.0	0.89	1878	0.0276
	-75	3.33	0.0041	11.5	0.85	1505	0.0288
	-80	3.42	0.0039	10.9	0.83	1395	0.0313
	-85	3.44	0.0044	10.5	0.85	1136	0.0317
	-90	3.47	0.0046	10.0	0.87	954	0.0354
	-95	3.32	0.0051	9.1	0.91	699	0.0355
	-100	3.39	0.0039	8.8	0.79	509	0.0402
	-105	3.41	0.0047	7.6	0.81	290	0.0423
	-110	3.36	0.0051	6.9	0.83	174	0.0447
	-115	3.40	0.0056	6.1	0.78	86	0.046
	-120	3.42	0.0053	5.9	0.81	—	—
	0	3.30	0.005	24.7	0.83	5024	0.0010
	-5	3.29	0.0045	23.2	0.82	5000	0.0021
	-10	3.31	0.0047	22.1	0.81	4289	0.0084
	-15	3.40	0.0052	20.8	0.85	3805	0.013
	-20	3.36	0.0044	19.2	0.81	3009	0.0149
	-25	3.42	0.0052	18.0	0.88	2527	0.0173
	-30	3.27	0.0056	16.3	0.91	2325	0.0210
	-35	3.30	0.0061	15.5	0.92	1820	0.0253
	-40	3.29	0.0058	14.2	0.88	1672	0.028
	-45	3.31	0.0049	13.8	0.85	1307	0.0298
	-50	3.40	0.0044	12.7	0.83	1292	0.033
	-55	3.32	0.0055	12.0	0.82	956	0.037
EG-Pt/CoP - 1.0	-60	3.29	0.0045	11.4	0.88	754	0.041
	-65	3.26	0.0041	10.7	0.8	697	0.045
	-70	3.40	0.0043	10.0	0.82	517	0.047
	-75	3.36	0.0047	9.1	0.83	365	0.0506
	-80	3.28	0.0053	8.3	0.88	258	0.0547
	-85	3.34	0.0052	8.0	0.81	164	0.0591
	-90	3.31	0.0042	7.2	0.89	78	0.062
	-95	3.33	0.0046	6.9	0.83	—	—

	0	3.41	0.0055	25.2	0.85	4363	0.0065
	-5	3.42	0.006	24.9	0.83	3103	0.0092
	-10	3.37	0.0057	23.6	0.82	2506	0.0181
	-15	3.44	0.0058	22.1	0.85	2134	0.0341
	-20	3.36	0.0062	20.2	0.9	1705	0.0475
	-25	3.33	0.007	19.1	0.92	1192	0.058
EG-Pt/CoP-1.5	-30	3.40	0.006	17.8	0.86	890	0.067
	-35	3.41	0.0049	16.6	0.81	735	0.076
	-40	3.38	0.0054	15.1	0.83	467	0.087
	-45	3.44	0.0056	13.9	0.86	286	0.102
	-50	3.33	0.0055	12.6	0.82	161	0.110
	-55	3.31	0.006	11.6	0.83	73	0.114
	-60	3.35	0.0054	10.0	0.86	—	—
	0	3.3	0.0051	25.0	0.89	3189	0.0106
	-5	3.32	0.0061	23.7	0.87	1915	0.0134
	-10	3.41	0.0049	22.6	0.88	1294	0.0248
	-15	3.31	0.006	20.2	0.86	1013	0.050
	-20	3.37	0.0046	18.9	0.81	736	0.0698
	-25	3.36	0.0055	17.7	0.88	611	0.0835
	-30	3.50	0.0066	16.5	0.9	408	0.0963
EG-Pt/CoP-3.0	-35	3.33	0.0044	14.7	0.83	324	0.113
	-40	3.40	0.0051	13.7	0.86	215	0.123
	-45	3.45	0.0046	12.1	0.82	125	0.130
	-50	3.40	0.006	10.7	0.9	55	0.135
	-55	3.36	0.0054	9.2	0.86	—	—

Calculation of H* coverage (Θ_{Pt}) values:

Integrating the obtained C_φ *vs.* η profiles in Fig. 2a and 2b presents the total H* adsorption charge for the Pt/CoP ($Q_{Total:\ Pt/CoP}$) and EG-Pt/CoP ($Q_{Total:\ EG\text{-}Pt/CoP}$) catalysts during HER. As references, the total H* adsorption charge for CoP ($Q_{\text{Total: CoP}}$) and CoP-EG ($Q_{Total:\ EG\text{-}CoP}$) are also calculated. Thus, the total H* adsorption charge on Pt for Pt/CoP ($Q_{Total\text{-}Pt:\ Pt/CoP}$) and EG-Pt/CoP ($Q_{Total\text{-}Pt:\ EG\text{-}Pt/CoP}$) in HER can be obtained from the difference value of $Q_{Total:\ Pt/CoP} - Q_{CoP}$ and $Q_{EG\text{-}Pt/CoP} - Q_{EG\text{-}CoP}$. Assuming that all loaded Pt nanoparticles (NPs) in the hybrid catalysts contribute to the H* adsorption in HER, the H* adsorption charge on unit area of Pt for Pt/CoP ($Q_{Unit\text{-}Pt:\ Pt/CoP}$) and EG-Pt/CoP ($Q_{Unit\text{-}Pt:\ EG\text{-}Pt/CoP}$) catalysts during HER can be estimated by:

$$Q_{Unit-Pt:\ Pt/CoP} = \frac{Q_{Total-Pt:\ Pt/CoP}}{Total\ surface\ area\ of\ loaded\ Pt\ in\ Pt/CoP\ catalysts\left(S_{Total-Pt:\ Pt/CoP}\right)} \text{ and;}$$

$$Q_{Unit-Pt:\ EG-Pt/CoP} = \frac{Q_{Total-Pt:\ Pt/CoP}}{Total\ surface\ area\ of\ loaded\ Pt\ in\ EG-Pt/CoP\ catalysts\left(S_{Total-Pt:\ Pt/CoP}\right)},$$

where $S_{Total\text{-}Pt:\ Pt/CoP}$ and $S_{Total\text{-}Pt:\ EG\text{-}Pt/CoP}$ at various Pt loading can be calculated as follows:

Mass of loaded catalysts (m_{cat}) in working electrode:

$$m_{cat} = 4mg \times \frac{5\mu L}{1000\mu L} = 0.02mg$$

Density of Pt (ρ_{Pt}): 21.5 g/cm^3

Total surface area of loaded Pt NPs:

$$S_{Total-Pt} = Total\ number\ of\ loaded\ Pt\ NPs \times Surface\ area\ of\ single\ Pt\ NPs$$

$$= \frac{Total\ volume\ of\ loaded\ Pt\ NPs}{Volume\ of\ single\ Pt\ NPs} \times 4\pi R_{Pt}^{\ 2}$$

$$= \frac{\frac{Mass\ of\ loaded\ Pt(m_{Pt})}{\rho_{Pt}}}{\frac{4}{3}\pi R_{Pt}^{\ 3}} \times 4\pi R_{Pt}^{\ 2} = \frac{3m_{Pt}}{\rho_{Pt} R_{Pt}}$$

For Pt/CoP-0.5:

Mass of loaded Pt nanoparticles for HER:

m_{Pt} = 0.02 mg × 0.46 % (From Table S1) = 9.2×10^{-8} g

Radius of Pt nanoparticles:

R_{Pt} = 0.79 nm (From Fig. S12)

Surface area of Pt:

$S_{Total\text{-}Pt} \approx 0.165$ cm^2

For Pt/CoP-1.0:

Mass of loaded Pt nanoparticles for HER:

m_{Pt} = 0.02 mg × 0.99 % (From Table S1) = 1.98×10^{-7} g

Radius of Pt nanoparticles:

R_{Pt} = 0.795 nm (From Fig. S12)

Surface area of Pt:

$S_{Total\text{-}Pt} \approx 0.347$ cm^2

For Pt/CoP-1.5:

Mass of loaded Pt nanoparticles for HER:

m_{Pt} = 0.02 mg × 1.47 % (From Table S1) = 2.94×10^{-7} g

Radius of Pt nanoparticles:

R_{Pt} = 0.8 nm (From Fig. S12)

Surface area of Pt:

$S_{Total\text{-}Pt} \approx 0.510$ cm^2

For Pt/CoP-3.0:

Mass of loaded Pt nanoparticles for HER:

m_{Pt} = 0.02 mg × 2.94 % (From Table S1) = 5.88×10^{-7} g

Radius of Pt nanoparticles:

R_{Pt} = 0.795 nm (From Fig. S12)

Surface area of Pt:

$S_{Total\text{-}Pt} \approx 1.00$ cm^2

For EG-Pt/CoP -0.5:

Mass of loaded Pt nanoparticles for HER:

m_{Pt} = 0.02 mg × 0.45 % (From Table S1) = 9.0×10^{-8} g

Radius of Pt nanoparticles:

R_{Pt} = 0.785 nm (From Fig. S6)

Surface area of Pt:
$S_{Total\text{-}Pt} \approx 0.160\ cm^2$

For EG-Pt/CoP -1.0:
Mass of loaded Pt nanoparticles for HER:
$m_{Pt} = 0.02\ mg \times 0.98\ \%$ (From Table S1) $= 1.96 \times 10^{-7}\ g$
Radius of Pt nanoparticles:
$R_{Pt} = 0.78\ nm$ (From Fig. S6)
Surface area of Pt:
$S_{Total\text{-}Pt} \approx 0.350\ cm^2$

For EG-Pt/CoP-1.5:
Mass of loaded Pt nanoparticles for HER:
$m_{Pt} = 0.02\ mg \times 1.45\ \%$ (From Table S1) $= 2.90 \times 10^{-7}\ g$
Radius of Pt nanoparticles:
$R_{Pt} = 0.77\ nm$ (From Fig. 1)
Surface area of Pt:
$S_{Total\text{-}Pt} \approx 0.510\ cm^2$

For EG-Pt/CoP -3.0:
Mass of loaded Pt nanoparticles for HER:
$m_{Pt} = 0.02\ mg \times 2.93\ \%$ (From Table S1) $= 5.86 \times 10^{-7}\ g$
Radius of Pt nanoparticles:
$R_{Pt} = 0.77\ nm$ (From Fig. S6)
Surface area of Pt:
$S_{Total\text{-}Pt} \approx 1.00\ cm^2$

By assuming the H adsorption charge for a monolayer is the same as that for a Pt (111) surface, i.e. $Q_{standard}$ = 210 μC/cm^2, the apparent H* coverage of Pt for Pt/CoP ($\Theta_{Pt:\ Pt/CoP}$) and EG-Pt/CoP ($\Theta_{Pt:\ EG\text{-}Pt/CoP}$) in equivalent monolayers of H* could be calculated as follow:
$\Theta_{Pt:\ Pt/CoP} = Q_{Unit\text{-}Pt:\ Pt/CoP}/210\ \mu C \cdot cm^{-2}$ and,
$\Theta_{Pt:\ EG\text{-}Pt/CoP} = Q_{Unit\text{-}Pt:\ EG\text{-}Pt/CoP}/210\ \mu C \cdot cm^{-2}$.
All calculated parameters were presented in Table S5 and S6.

Table S5. Parameters in Θ_{Pt} calculations for the Pt/CoP catalysts and CoP reference during HER.

Parameters \ Catalysts	CoP	Pt/CoP-0.5	Pt/CoP-1.0	Pt/CoP-1.5	Pt/CoP-3.0
Q_{Total} (μC)	2142	2181	2225	2266	2350
$Q_{Total\text{-}Pt}$ (μC)	—	39	83	124	208
$S_{Total\text{-}Pt}$ (cm^2)	—	0.165	0.347	0.510	1.00
$Q_{Unit\text{-}Pt}$ (μC/cm^2)	—	236	239	243	208
Θ_{Pt}	—	1.1	1.1	1.2	1.0

Table S6. Parameters in Θ_{Pt} calculations for the EG-Pt/CoP catalysts and EG-CoP reference during HER.

Parameters \ Catalysts	EG-CoP	EG-Pt/CoP-0.5	EG-Pt/CoP-1.0	EG-Pt/CoP-1.5	EG-Pt/CoP-3.0
Q_{Total} (μC)	2200	2463	2793	3347	3877
$Q_{Total\text{-}Pt}$ (μC)	—	263	593	1147	1747
$S_{Total\text{-}Pt}$ (cm^2)	—	0.16	0.35	0.51	1.0
$Q_{Unit\text{-}Pt}$ (μC/cm^2)	—	1643	1694	2249	1677
Θ_{Pt}	—	8	8.2	10.7	7.9

Table S7. The integral for PDOS of $Pt_{(I)}$ d-band.

Catalysts / d-band	Pt/CoP	EG-Pt/CoP
d_{xy}	1.47	1.48
d_{yz}	1.69	1.43
d_{xz}	1.43	1.54
d_{z^2}	1.69	1.81
$d_{x^2-y^2}$	1.62	1.48

Table S8. Comparison of HER performance in acidic media for EG-Pt/CoP-1.5 with the state-of-the-art hydrogen spillover electrocatalysts.

Catalyst	η_{10} [mV]	η_{100} [mV]	j_0 [mA/cm^2]	Tafel slope [mV/dec]	Catalyst loading [mg/cm^2]	Noble metal loading [mg/cm^2]	Duability [h]	Ref
EG-Pt/CoP-1.5	21	108	1.67	42.5	0.102	0.001	100	This work
Rh/SiNWs	81	180	0.009	24	0.193	0.056	138	Ref. 18
Rh/MoS_2	47	141	0.114	24	0.31	0.016	22.2	Ref. 19
Rh/Si/C	36	108	0.909	26	—	0.009	5	Ref. 20
Rh/Au/Si	65	168	0.048	24	0.255	0.08	2	Ref. 21
Rh/Ag/Si	121	—	0.087	51	0.14	0.04	12	Ref. 22
Pt/Au	32	—	—	30	—	—	6	Ref. 23
Pt/Au/Si	56	156	—	24	0.092	0.04	10	Ref. 24
Ir/Si	22	—	0.946	20	0.339	0.06	14	Ref. 25
Ir/Au/Si	40	114	—	24	0.283	0.06	17.5	Ref. 26
Pt/WO_3	42	—	—	73	—	0.016	19.4	Ref. 27
WO_2/WS_2	100	152	0.137	54	—	0	3.1	Ref. 28
rGO/WS_2/WO_3	113	—	—	37	0.71	0	16	Ref. 29

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