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Electronic Supplementary Information

Fabrication of a 3D self-supporting Ni-P/Ni_2P/CC composite and their robust hydrogen evolution reaction property in alkaline solution

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Supplementary Methods

Calculation of the number of active sites and turnover frequency (TOF)

The number of active sites (*n*) was determined by CV with a potential window from -0.2 to 0.6 V vs. RHE in 1.0 M PBS (pH = 7) at a scan rate of 50 mV s^{-1}. Assuming a one-electron process for both reduction and oxidation, the upper limit of *n* could be calculated[1] according to the equation (S1):

$$n = \frac{Q}{2F} \tag{S1}$$

Where Q is the voltammetric charge obtained by integrating the CV curves, F is the Faradic constant (96485 C mol^{-1}).

Then, the turnover frequency (TOF, s^{-1}) was defined[2] via the following equation (S2):

$$\mathrm{TOF} = \frac{j \times A}{2nF} \tag{S2}$$

Where j is the current density (A cm^{-2}) at a specific overpotential, A is the area of the electrode (cm^2), and n is the number of active sites (mol).

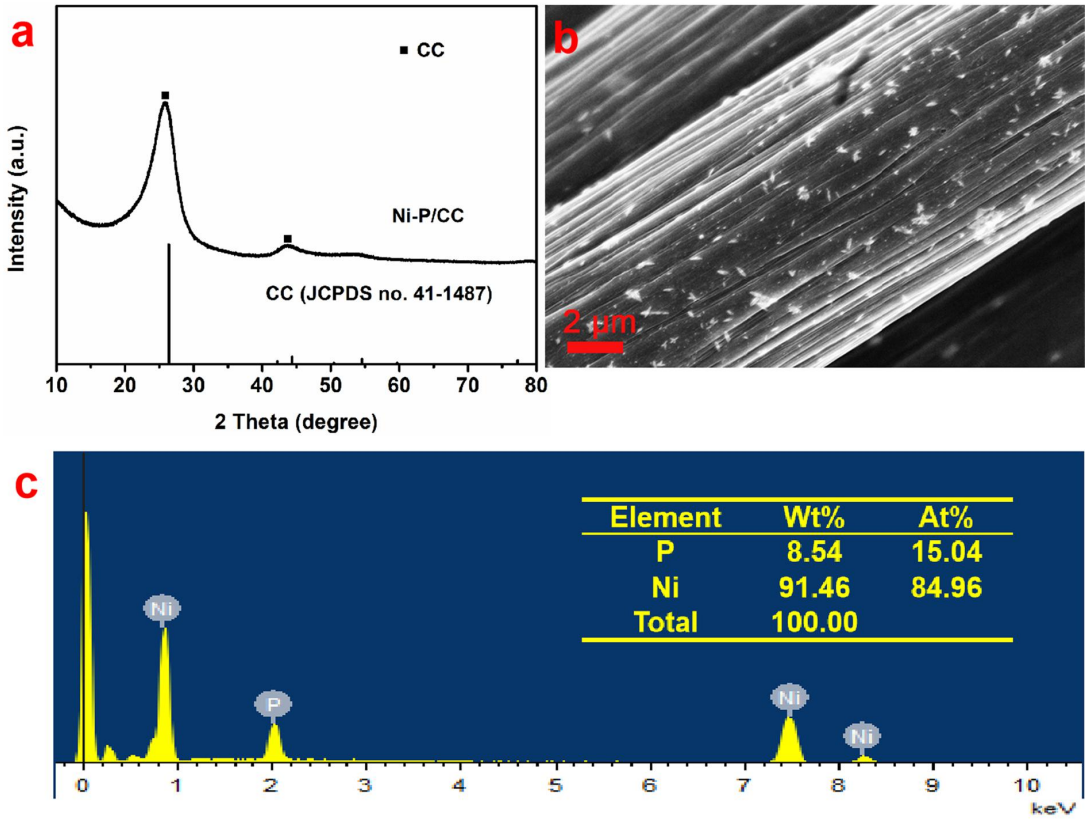

Fig. S1 (a) XRD pattern of Ni-P/CC, (b) SEM image of Ni-P/CC and (c) EDS spectrum of Ni-P/CC with the deposition time of 120 s at the current density of 1 mA cm^{-2}.

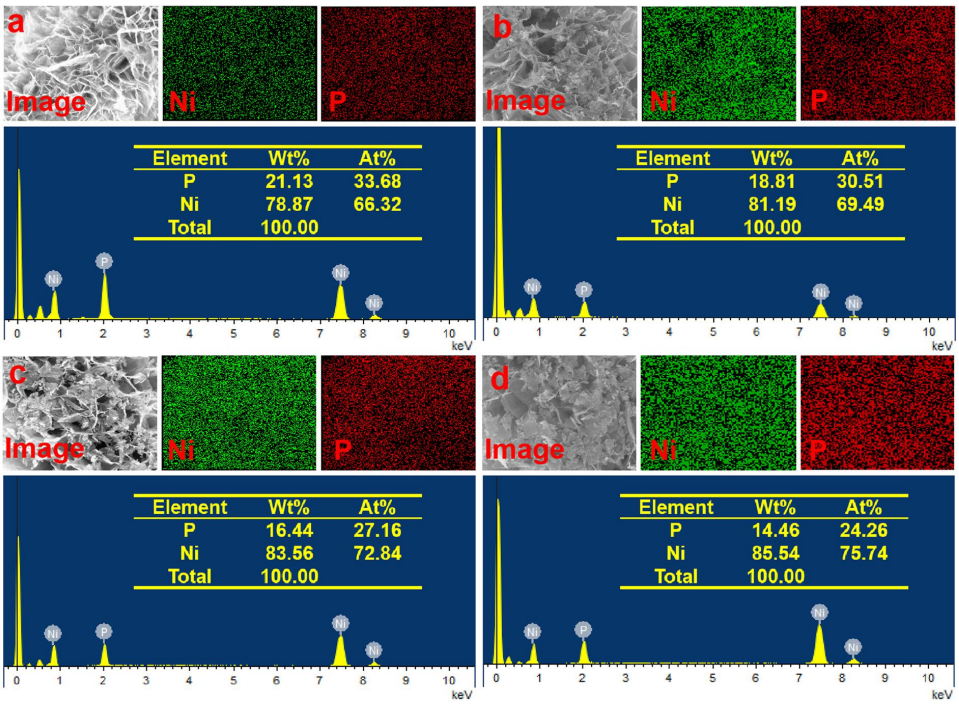

Fig. S2 EDS spectrum of (a) Ni_2P/CC, (b) Ni-P/Ni_2P/CC-1, (c) Ni-P/Ni_2P/CC-2 and (d) Ni-P/Ni_2P/CC-3.

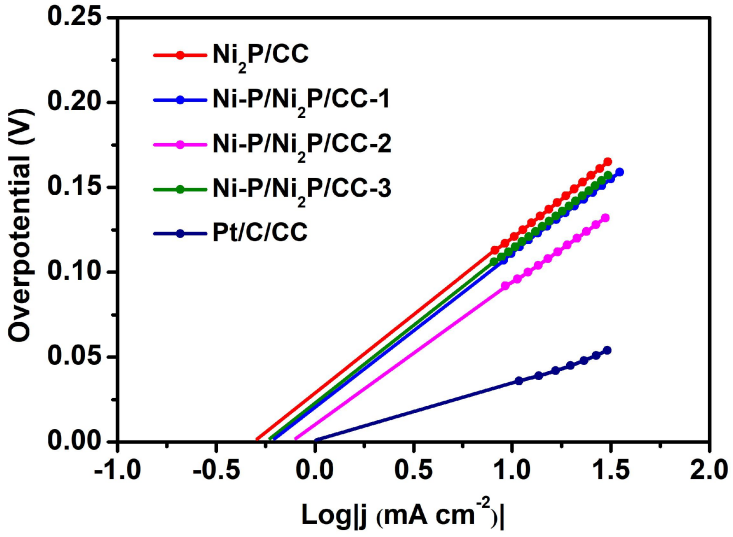

Fig. S3 Calculated exchange current density for Ni_2P/CC, Ni-P/Ni_2P/CC-1, Ni-P/Ni_2P/CC-2, Ni-P/Ni_2P/CC-3, and Pt/C/CC in 1.0 M KOH solution by applying extrapolation of Tafel plot data.

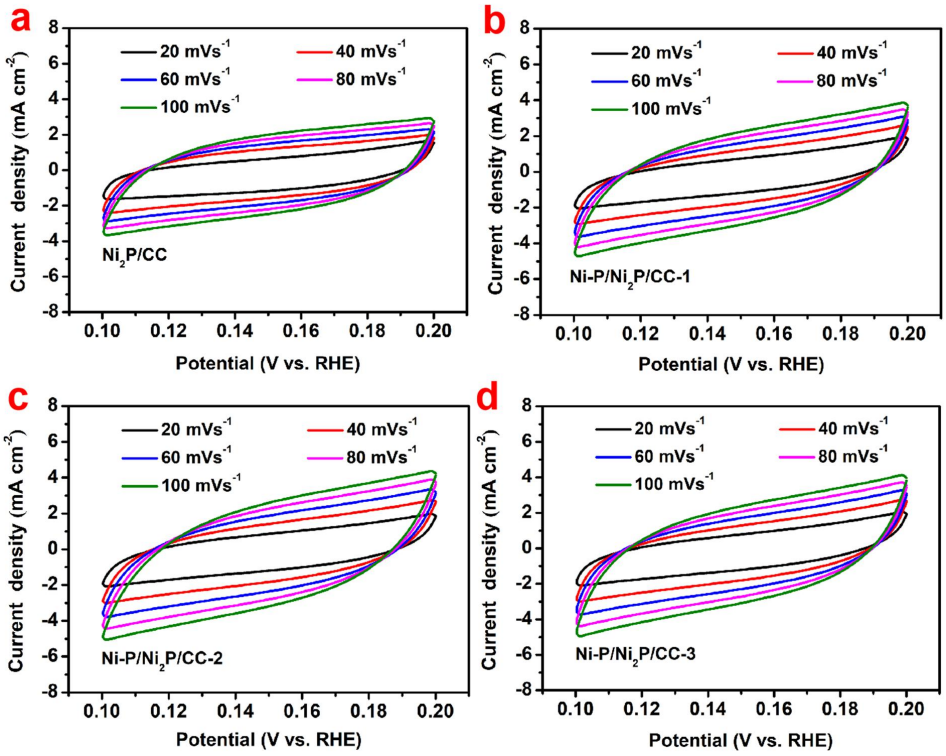

Fig. S4 CV curves of (a) Ni_2P/CC, (b) Ni-P/Ni_2P/CC-1, (c) Ni-P/Ni_2P/CC-2 and (d) Ni-P/Ni_2P/CC-3 in 1.0 M KOH solution at different scan rates.

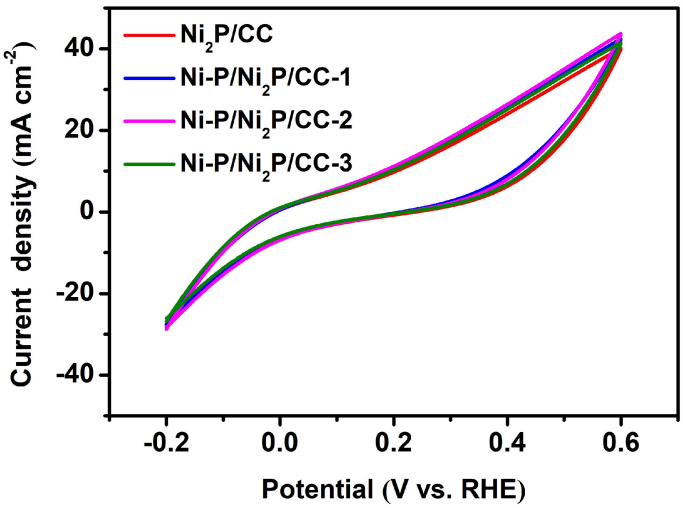

Fig. S5 CV curves of Ni_2P/CC, Ni-P/Ni_2P/CC-1, Ni-P/Ni_2P/CC-2 and Ni-P/Ni_2P/CC-3 in 1 M PBS (pH = 7) with a scan rate of 50 mV s^{-1}.

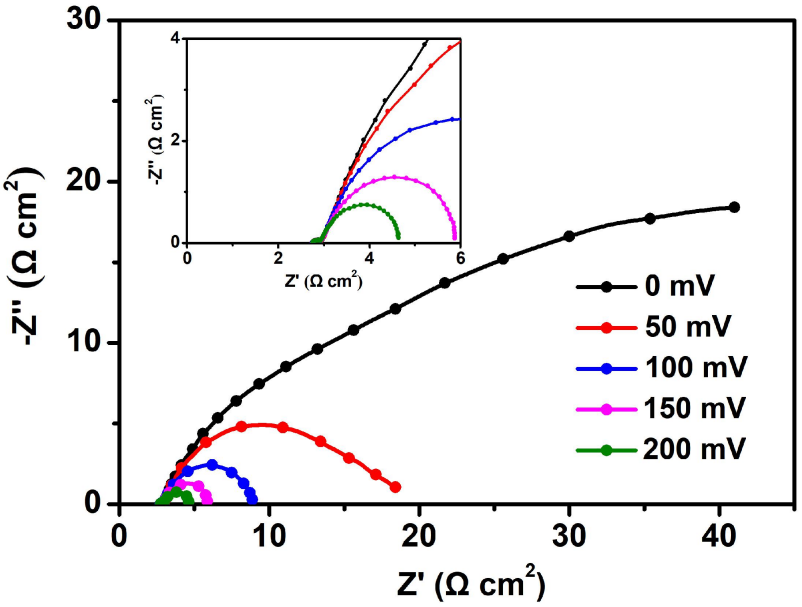

Fig. S6 Nyquist plots of Ni-P/Ni_2P/CC-2 composite at different overpotential values.

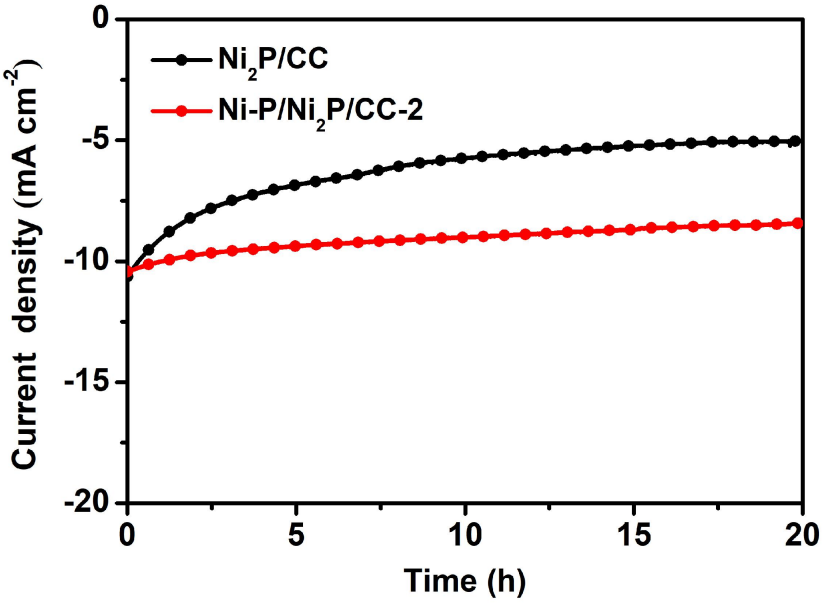

Fig. S7 Time-dependent current density curve of Ni_2P/CC and Ni-P/Ni_2P/CC-2 at a constant overpotential for 20 h in 1.0 M KOH solution.

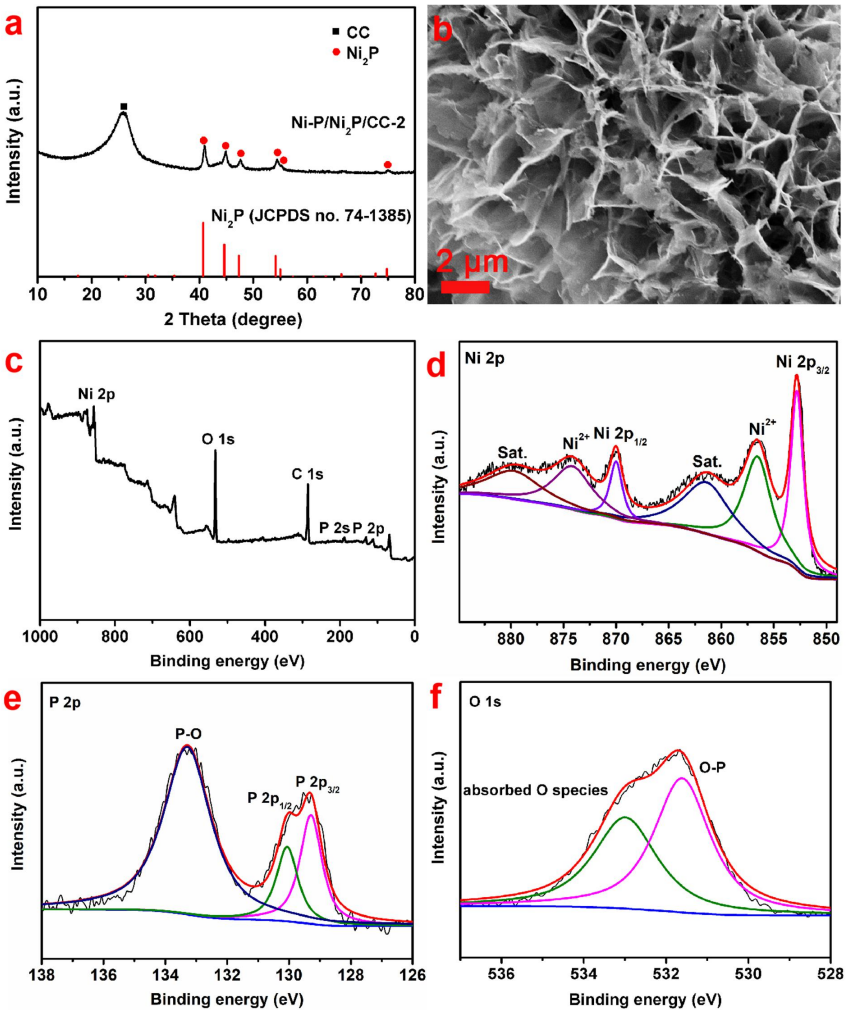

Fig. S8 (a) XRD pattern, (b) SEM image and (c-f) XPS spectra of Ni-P/Ni_2P/CC-2 after long-term stability test in 1.0 M KOH solution.

Table S1 ICP-OES data for Ni-P/CC, Ni_2P/CC, Ni-P/Ni_2P/CC-1, Ni-P/Ni_2P/CC-2 and Ni-P/Ni_2P/CC-3 samples.

Catalyst	Ni (mg cm^{-2})	P (mg cm^{-2})	Ni/P atomic ratio
Ni-P/CC	0.033	0.003	5.80
Ni_2P/CC	3.073	0.794	2.04
Ni-P/Ni_2P/CC-1	3.178	0.706	2.37
Ni-P/Ni_2P/CC-2	3.289	0.614	2.82
Ni-P/Ni_2P/CC-3	3.367	0.550	3.23

Table S2 Analyzed parameters of the EIS data for Ni_2P/CC, Ni-P/Ni_2P/CC-1, Ni-P/Ni_2P/CC-2 and Ni-P/Ni_2P/CC-3 samples.

Catalyst	R_s (Ω cm^2)	Y_1 (F cm^{-2} s$^{(n-1)}$)	n_1	R_1 (Ω cm^2)	Y_2 (F cm^{-2} s$^{(n-1)}$)	n_2	R_{ct} (Ω cm^2)
Ni_2P/CC	2.44	5.08×10^{-4}	0.742	0.95	1.22×10^{-2}	0.954	4.11
Ni-P/Ni_2P/CC-1	2.48	9.63×10^{-2}	0.375	0.41	1.54×10^{-2}	0.952	3.31
Ni-P/Ni_2P/CC-2	2.76	3.80×10^{-2}	0.521	0.34	2.03×10^{-2}	0.948	2.81
Ni-P/Ni_2P/CC-3	2.65	8.81×10^{-2}	0.511	0.52	1.26×10^{-2}	0.994	3.46

Table S3 Comparison of the HER performances in 1.0 M KOH solution among several reported Ni-based catalysts (GCE is glassy carbon electrode).

Catalyst	Substrates	η_{10} (mV)	Tafel slope (mV dec^{-1})	Ref.
Ni-P/Ni_2P/CC-2	Carbon cloth	95	80.4	This work
Mn-NiP_2 NSs/CC	Carbon cloth	97	61	3
Ni_2P-Ni_5P_4	Carbon cloth	102	83	4
CP@Ni-P	Carbon paper	117	85.4	5
O3-V10-Ni_2P	GCE	108	72.3	6
Ni_2P/FeP@NG	GCE	250	91	7
Ni_2P/MoS_2/N:RGO	GCE	149	60.2	8
Al-Ni_2P/TM	Ti mesh	129	98	9
Ni_2P/Ni/NF	Ni foam	98	72	10
Cu_3P-Ni_2P/NF	Ni foam	103	80	11
P-Ni_2P/NF	Ni foam	134	92	12

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