Electronic Supplementary Information (ESI)

Shape effects of nickel phosphide nanocrystals on the hydrogen evolution reaction

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1. Supplementary Notes

1.1 Measurement of electrochemically active surface area (ECSA). The ECSA was determined from the double layer capacitance (C_{dl}) of the catalyst surface.[S1,S2] The C_{dl} was determined by measuring cyclic voltammograms (CVs) with multiple scan rates in non-faradaic potential region. In this potential region, all measured currents are assumed to be associated with double-layer charging. The potential range typically centred at the open-circuit potential (OCP) with a potential window of 0.1 V. In this work, CVs were measured in a potential range of (0.125-0.225 V vs. RHE) at the scan rates of (v =0.01, 0.02, 0.06, 0.08, 0.10, 0.15, and 0.20 mV s^{-1}). The measured charging current (i_c) is equal to the product of the scan rate (v) and the C_{dl}, as given by equation (1).

$$i_c = vC_{dl} \cdots\cdots (1)$$

Therefore, the slope derived from a plot of i_c as a function of v equal to the C_{dl} (Figure S3). The ECSA of a catalyst is calculated by dividing the C_{dl} with specific capacitance of the sample according to equation (2).

$$ECSA = \frac{C_{dl}}{C_s} \cdots\cdots (2)$$

Jaramillo et al suggest general specific capacitances of C_s based on typical reported values.[S1] In this work 0.035 mF cm^{-2} of C_s was used for ECSA calculations.

1.2 Calculation of turnover frequency (TOF). The turnover frequency (TOF, s^{-1}) defined as the HER rate per active site and per time, was derived from the following equation (3).

$$TOF(s^{-1}) = \left\{ i \times \frac{1H_2}{2e^-} \times \frac{1e^-}{q_e} \right\} / N_{active} \cdots\cdots (3)$$

Here, the current (i) was experimentally determined from electrochemical measurement, and q_e is the electron charge of 1.602×10^{-19} C. In this work, the current at −200 mV (*vs.* RHE) was used for TOF calculation. N_{active} is the number of active surface atoms. For determining N_{active}, the method proposed by previous works was employed.[S3,S4] The approach use average of the atoms in the molar volume to a surface, providing a crude upper bound for TOF values. The hexagonal unit cell for Ni_2P has a molar volume of:

$$V_m = \frac{F_w}{\rho} = \frac{148.36\ g/mol}{7.35\ g/cm^3} = \frac{20.1850\ cm^3}{1\ mol_{Ni_2P}}$$

The average surface occupancy is:

$$\left(\frac{1\ mol_{Ni_2P}}{20.1850\ cm^3} \times \frac{3 \times 6.022 \times 10^{23}\ atoms}{1\ mol_{Ni_2P}}\right)^{\frac{2}{3}} = 2.00 \times 10^{15}\,\frac{atoms}{cm^2}$$

The N_{active} was determined using the ECSA, which was derived from double layer capacitance measurement (See Experimental sections, and Figure S3),[S1] as described in the following equation:

$$N_{active} = ECSA\ (cm^2) \times 2.00 \times 10^{15}\frac{atoms}{cm^2}$$

Finally, the TOFs were calculated by integrating N_{active} into the Equation (2).

2. Supplementary Tables S1-S3

Table S1. The average length and diameter of Ni_2P NRs-S and NRs-L, and the diameter of Ni_2P NSs, determined by TEM images.

Sample	Diameter (nm) [a]	Length (nm) [a]
Ni_2P NSs	7.1 ± 1.0	-
Ni_2P NRs-S	5.3 ± 1.1	41 ± 10
Ni_2P NRs-L	4.0 ± 0.4	137 ± 47

[a] Crystallite sizes (diameter and length) were measured on the particles in TEM images. The values were obtained by averaging the measured sizes over one hundred of particles.

Table S2. HER activity of Ni_2P NPs, expressed in terms of overpotentials at 10 mA cm^{-2}, Tafel slopes, and exchange current densities values.

Sample	Overpotential at 10 mA cm^{-2} (V)	Tafel slope[a] (mV dec^{-1})	Exchange current density[b] (A cm^{-2})
Ni_2P NSs/CP	0.135	50	3.68×10^{-5}
Ni_2P NRs-L/CP	0.270	86	7.45×10^{-6}

[a,b] The Tafel slopes and exchange current densities were derived from the linear portion of the corresponding Tafel plots.

Table S3. Double layer capacitance, ECSA, and TOF values of Ni_2P-based catalysts.

Sample	Double layer capacitance[a] (C_{dl}, mF)	ECSA[b] (cm^2)	TOF[c] (s^{-1})
Ni_2P NSs/CP	3.2	91	0.63
Ni_2P NRs-L/CP	1.6	46	0.05

[a,b] Double layer capacitance and ECSA were determined via previous method.[S1,S2]

[c] TOF was determined by previous method (see Experimental section in manuscript).[S3,S4]

3. Supplementary Figs. S1-S6

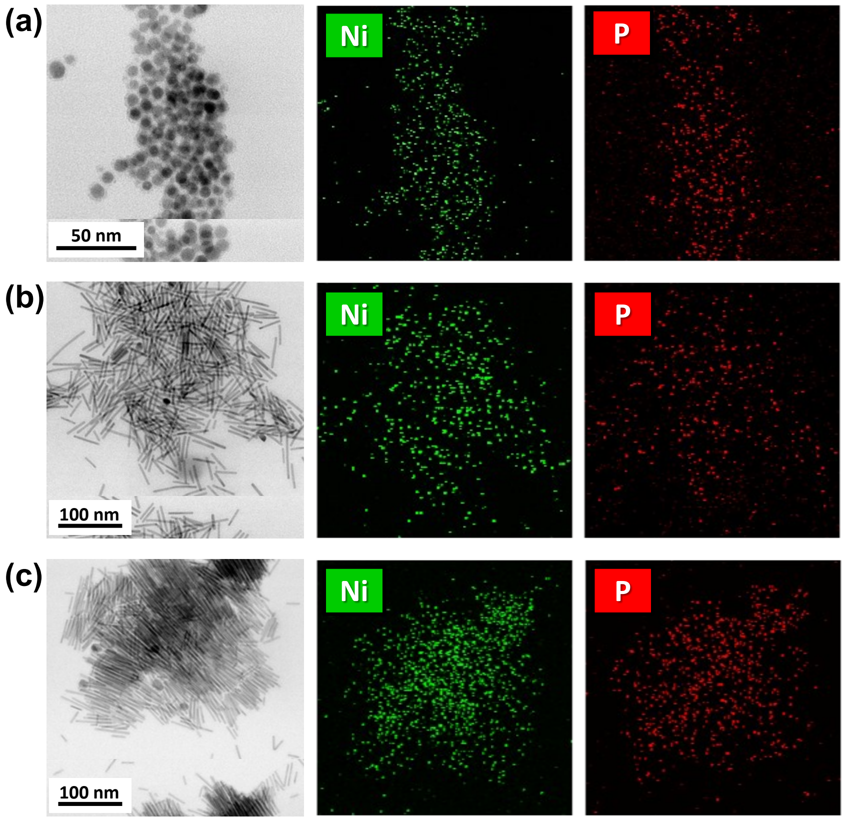

Fig. S1 EDS elemental mapping images of (a) Ni_2P NSs, (b) Ni_2P NRs-S, and (c) Ni_2P NRs-L samples.

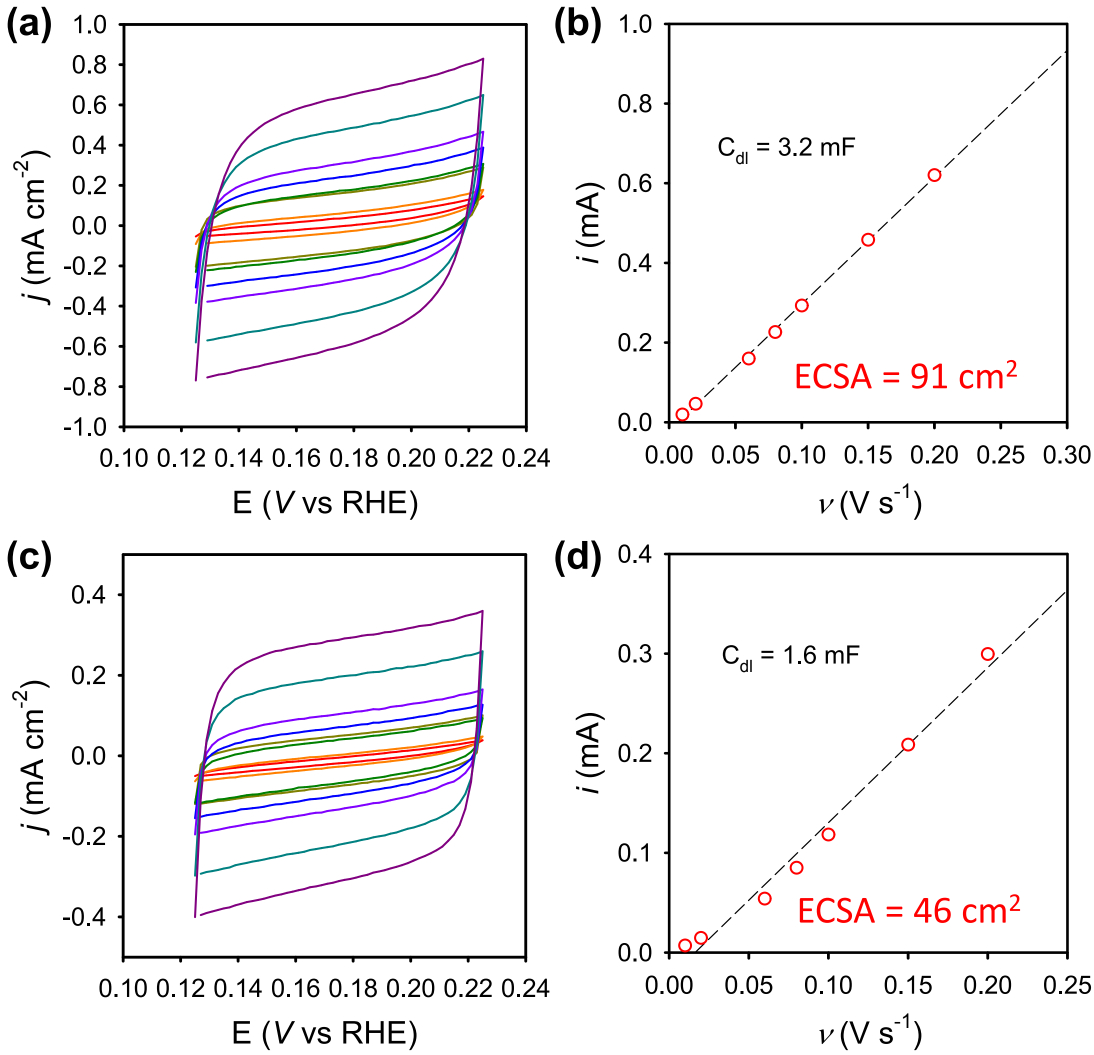

Fig. S2 Cycling voltammetry scans with different scan rate and corresponding linear plot for cathodic current versus scan rate for (a,b) Ni_2P NSs/CP and (c,d) Ni_2P NRs-L/CP catalysts. Double layer capacitance was determined from the linear plot.

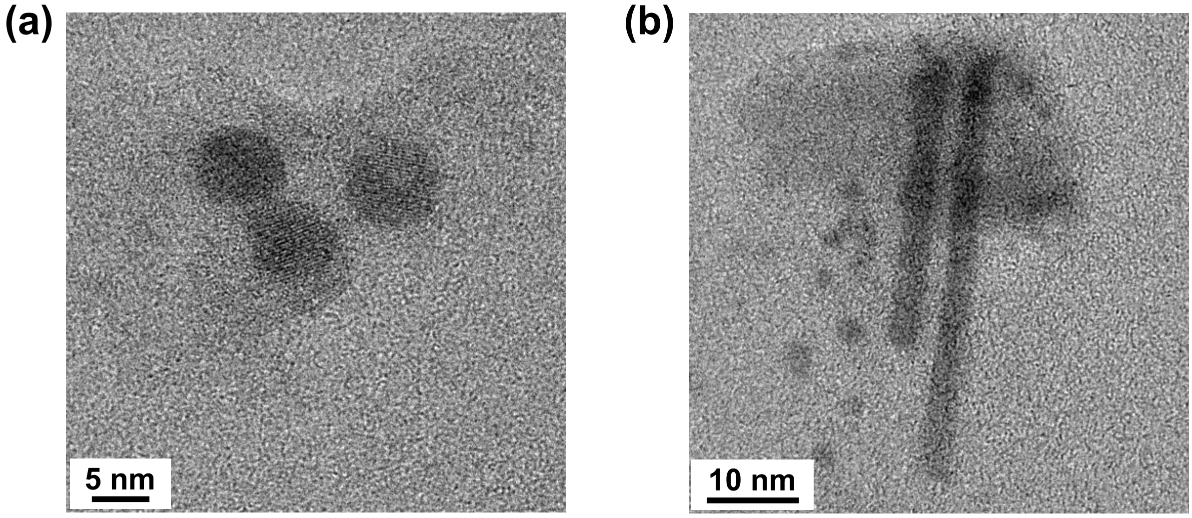

Fig. S3 TEM images of (a) Ni_2P NSs/CP and (b) Ni_2P NRs-L/CP after the chronopotentiometry measurements.

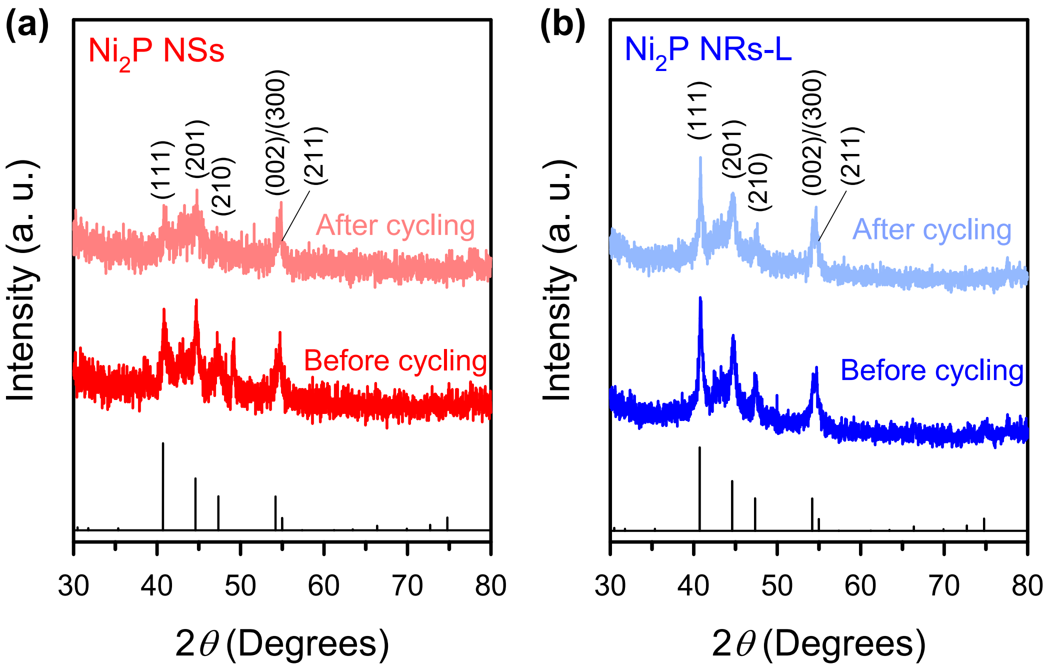

Fig. S4 XRD patterns of (a) Ni_2P NSs/CP and (b) Ni_2P NRs-L/CP recorded before and after 1,000 CV cycles in acidic media (0.5 M H2SO4). Vertical bars represent the XRD pattern for Ni2P standard (JCPDS No. 89-2742).

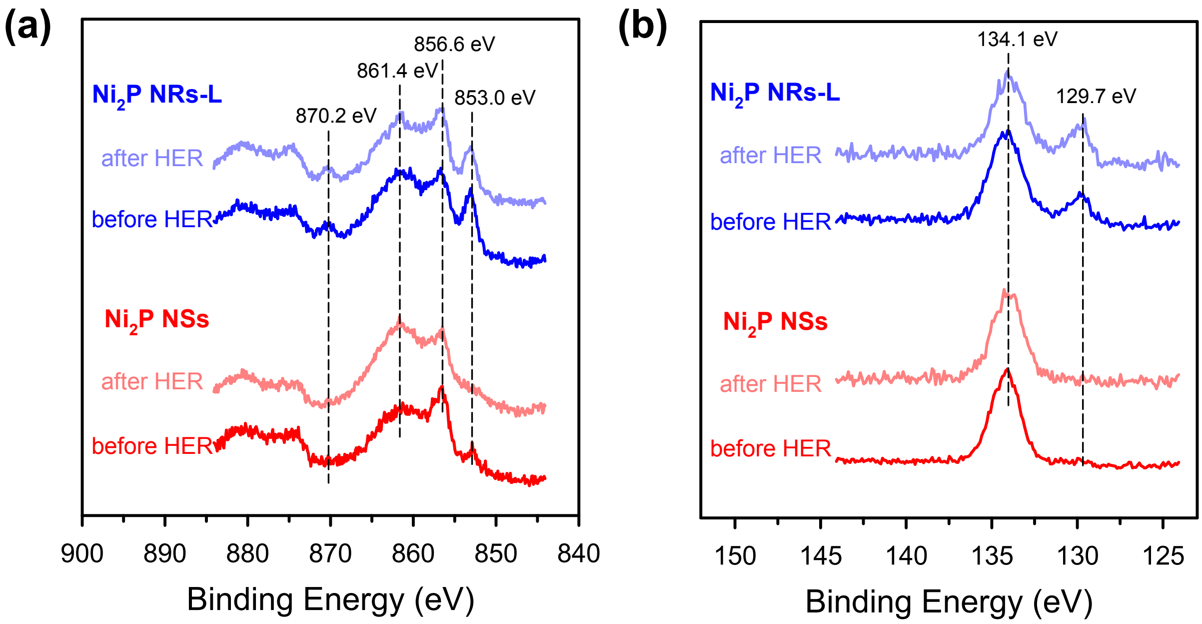

Fig. S5 (a) Ni 2p- and (b) P 2p XPS spectra for Ni_2P NPs/CP before and after 1,000 CV cycles in acidic media (0.5 M H_2SO_4).

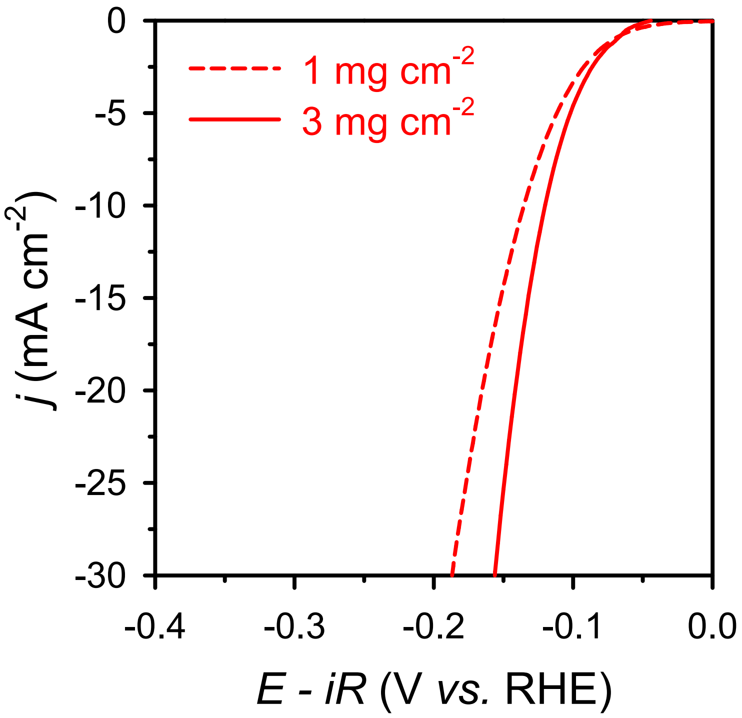

Fig. S6 Polarisation curves of Ni_2P NSs/CP for the HER with different catalyst loadings of 1 mg cm^{-2} and 3 mg cm^{-2}.

4. References for Supporting Information

S1. C. C. L. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2013, **135**, 16977-16987.

S2. C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2015, **137**, 4347-4357.

S3. E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, *J. Am. Chem. Soc*., 2013, **135**, 9267-9270.

S4. A. B. Laursen, K. R. Patraju, M. J. Whitaker, M. Retuerto, T. Sarkar, N. Yao, K. V. Ramanujachary, M. Greenblatt and G. C. Dismukes, *Energy Environ. Sci.*, 2015, **8**, 1027-1034.