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 \((0.125-0.225 \text{ V vs. RHE})\) at the scan rates of \((v =0.01, 0.02, 0.06, 0.08, 0.10, 0.15, \text{ and } 0.20 \text{ mV s}^{-1}\)). 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).

\[
 i_c = vC_{dl} \ldots \ldots (1)
\]

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).

\[
 ECSA = \frac{C_{dl}}{C_s} \ldots \ldots (2)
\]

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).

\[
 TOF(s^{-1}) = \left\{ \frac{i \times \frac{1H_2}{2e^-} \times \frac{1e^-}{q_e}}{N_{active}} \right\} \ldots \ldots (3)
\]

Here, the current \( i \) was experimentally determined from electrochemical measurement, and \( q_e \) is the electron charge of \( 1.602 \times 10^{-19} \text{ C} \). In this work, the current at \(-200 \text{ mV (vs. RHE)}\) 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\(_2\)P has a molar volume of:
\[
V_m = \frac{F_w}{\rho} = \frac{148.36 \text{ g/mol}}{\frac{7.35 \text{ g/cm}^3}{1 \text{ mol}_{Ni2P}}} = \frac{20.1850 \text{ cm}^3}{1 \text{ mol}_{Ni2P}}
\]

The average surface occupancy is:

\[
\left( \frac{1 \text{ mol}_{Ni2P}}{20.1850 \text{ cm}^3} \times \frac{3 \times 6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}_{Ni2P}} \right)^2 = 2.00 \times 10^{15} \frac{\text{ atoms}}{\text{ cm}^2}
\]

The \( N_{active} \) was determined using the ECSA, which was derived from double layer capacitance measurement (See Experimental sections, and Figure S3),\(^{51} \) as described in the following equation:

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

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$_2$P NRs-S and NRs-L, and the diameter of Ni$_2$P NSs, determined by TEM images.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter (nm)$^a$</th>
<th>Length (nm)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$P NSs</td>
<td>7.1 ± 1.0</td>
<td>-</td>
</tr>
<tr>
<td>Ni$_2$P NRs-S</td>
<td>5.3 ± 1.1</td>
<td>41 ± 10</td>
</tr>
<tr>
<td>Ni$_2$P NRs-L</td>
<td>4.0 ± 0.4</td>
<td>137 ± 47</td>
</tr>
</tbody>
</table>

$^a$ 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$_2$P NPs, expressed in terms of overpotentials at 10 mA cm$^{-2}$, Tafel slopes, and exchange current densities values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Overpotential at 10 mA cm$^{-2}$ (V)</th>
<th>Tafel slope$^a$ (mV dec$^{-1}$)</th>
<th>Exchange current density$^b$ (A cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$P NSs/CP</td>
<td>0.135</td>
<td>50</td>
<td>3.68 x 10$^{-5}$</td>
</tr>
<tr>
<td>Ni$_2$P NRs-L/CP</td>
<td>0.270</td>
<td>86</td>
<td>7.45 x 10$^{-6}$</td>
</tr>
</tbody>
</table>

$^a,b$ 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$_2$P-based catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Double layer capacitance$^a$ ($C_{dl}$, mF)</th>
<th>ECSA$^b$ (cm$^2$)</th>
<th>TOF$^c$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$P NSs/CP</td>
<td>3.2</td>
<td>91</td>
<td>0.63</td>
</tr>
<tr>
<td>Ni$_2$P NRs-L/CP</td>
<td>1.6</td>
<td>46</td>
<td>0.05</td>
</tr>
</tbody>
</table>

$^a,b$ Double layer capacitance and ECSA were determined via previous method.$^{S1,S2}$

$^c$ TOF was determined by previous method (see Experimental section in manuscript).$^{S3,S4}$
Fig. S1 EDS elemental mapping images of (a) Ni$_2$P NSs, (b) Ni$_2$P NRs-S, and (c) Ni$_2$P 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$_2$P NSs/CP and (c,d) Ni$_2$P NRs-L/CP catalysts. Double layer capacitance was determined from the linear plot.
Fig. S3 TEM images of (a) Ni$_2$P NSs/CP and (b) Ni$_2$P NRs-L/CP after the chronopotentiometry measurements.
Fig. S4 XRD patterns of (a) Ni$_2$P NSs/CP and (b) Ni$_2$P NRs-L/CP recorded before and after 1,000 CV cycles in acidic media (0.5 M H$_2$SO$_4$). Vertical bars represent the XRD pattern for Ni$_2$P standard (JCPDS No. 89-2742).
Fig. S5 (a) Ni 2p- and (b) P 2p XPS spectra for Ni$_2$P NPs/CP before and after 1,000 CV cycles in acidic media (0.5 M H$_2$SO$_4$).
Fig. S6 Polarisation curves of Ni$_2$P NSs/CP for the HER with different catalyst loadings of 1 mg cm$^{-2}$ and 3 mg cm$^{-2}$.
4. References for Supporting Information


