Electronic Supplementary Materials

Fe$_2$P/reduced graphene oxide/Fe$_2$P sandwich-structured nanowall arrays: a high-performance non-noble-metal electrocatalyst for hydrogen evolution

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Fig. S1 CV curves for electrolyzing (a) colloidal solution of GO, (b) the Fe precursor composed of FeSO$_4$ and Na$_2$S$_2$O$_3$, and (c) GO/Fe precursor colloidal solution on Ti plates performed in the potential range between −1.4 and 0.6 V versus SCE for 20 cycles. The arrows point to the increase of the peak current densities, meaning the deposition of the conductive materials.
**Fig. S2** Histogram of statistical analysis of Fe$_2$P particle size (based on 100 randomly picked particles).

**Fig. S3** (a) EDX and (b) XRD pattern of FeO$_x$@rGO.
Fig. S4 Raman spectrum of Fe$_2$P@rGO, rGO-T and rGO. The D and G bands are indicative of the graphene moiety.

Fig. S5 (a) Polarization curves and (b) corresponding Tafel plots for the different materials in N$_2$-saturated 1.0 M NaOH solution at a scan rate of 2 mV s$^{-1}$;
Fig. S6 Cyclic voltammetry curves of (a) Fe$_2$P@rGO and (b) Fe$_2$P in the range of 0-0.14 V vs. RHE. The scan rate is 40, 80, 120, 160, 200, 240, and 300 mV s$^{-1}$ for the curves from inside to outside.
As shown in Fig. S7, $R_s$ represents the ohmic resistance arising from the electrolyte and all contacts. The time constant $R_1$-CPE may relate to the interfacial resistance resulting from the electron transport between the catalyst and the Ti plate, the higher CPE can further indicate the specific surface area of Fe$_2$P@rGO (Table S1). $Q$ and $R_{ct}$ are assigned as the double-layer capacitance and charge-transfer resistance at the interface between the catalyst and the electrolyte, which generally represents the electrochemical activity of the electrode.

Fig. S7 Equivalent circuit used for fitting the Nyquist plots in Figure 4d.

![Equivalent circuit](image)

Fig. S8 (a) Current-time curve of Fe$_2$P@rGO in 0.5 M H$_2$SO$_4$ solution at an overpotential of 300 mV for 12 h (b) XPS spectra of P 2p before and after 5000 cycles test.
Fig. S9 (a) SEM images and (b) XRD pattern of Fe$_2$P@rGO after 5000 cycles test.
**Calculation of active sites**

The number of active sites are calculated from the cyclic voltammograms without faradic current in Figure S5 at the rate of 200 mV s$^{-1}$ by integrating the current over the whole potential. Later, the absolute components of the voltammetric charges (cathodic and anodic) reported during one single blank measurement were added. Assuming a one electron redox process, this absolute charge was divided by two. The value was then divided by the Faraday constant to get the number of active sites of the film. The total number of active sites for each catalyst can be calculated from cyclic voltammetry by integrating the current over the whole potential.

The number of active sites = Area under the curve / 2F

The calculated number of active sites for the electrode materials are,

\[ n \text{ (Fe}_2\text{P@rGO)} = 1.0 \times 10^{-3} \text{ mol g}^{-1} \]

\[ n \text{ (Fe}_2\text{P)} = 8.0 \times 10^{-5} \text{ mol g}^{-1} \]

**Determination of the turnover frequency (TOF)**

When the number of active sites is known, the turnover frequencies (in s$^{-1}$) were calculated with the following equation:

\[ \text{TOF} = \frac{j}{F n} \frac{1}{2} \]

\(j\): Current (in A) during the linear sweep measurement at \(\eta = 200 \text{ mV}\).

\(F\): Faraday constant (in C/mol).

\(n\): Number of active sites (in mol) calculated as the method above.

The factor \(\frac{1}{2}\) arrives by taking into account that two electrons are required to form one hydrogen molecule from two protons.
$$\text{TOF(Fe}_2\text{P@rGO)} = \frac{100.80 \text{ mA cm}^{-2}}{96485.34 \text{ C mol}^{-1} \times 1.0 \times 10^{-3} \text{ mol g}^{-1} \times 0.47 \text{ mg cm}^{-2} \times 2}$$

$$\text{TOF(Fe}_2\text{P)} = \frac{2.44 \text{ mA cm}^{-2}}{96485.34 \text{ C mol}^{-1} \times 8.0 \times 10^{-5} \text{ mol g}^{-1} \times 0.47 \text{ mg cm}^{-2}}$$

Table **S1**. Electrochemical impedance parameters obtained by fitting the Nyquist plots to the equivalent circuit model (Figure S6).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$R_s$ (Ω)</th>
<th>$C_1$ (mF cm$^{-2}$)</th>
<th>$R_1$ (Ω)</th>
<th>$Q$</th>
<th>$Y_1($Ω$^{-1}s^n)$</th>
<th>$n$</th>
<th>$R_{ct}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$P@rGO</td>
<td>19.67</td>
<td>0.163</td>
<td>286.8</td>
<td>7.403×10$^{-5}$</td>
<td>0.8864</td>
<td>248.4</td>
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<tr>
<td>Fe$_2$P</td>
<td>28.18</td>
<td>0.072</td>
<td>330.0</td>
<td>16.9×10$^{-5}$</td>
<td>0.8891</td>
<td>4563</td>
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</table>

Table **S2**. Comparison of HER activity of some transition metal phosphides.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Current density (mA·cm$^{-2}$)</th>
<th>Potential (mV)</th>
<th>Tafel slope (mV·dec$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$P@rGO</td>
<td>10</td>
<td>101</td>
<td>55.2</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>122</td>
<td></td>
<td></td>
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<tr>
<td>Fe-Co$_2$P/CNTs</td>
<td>10</td>
<td>104</td>
<td>58</td>
<td>1</td>
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<tr>
<td></td>
<td>10</td>
<td>165</td>
<td>68</td>
<td>2</td>
</tr>
<tr>
<td>Co$<em>{0.6}$Ni$</em>{0.4}$P/CNT</td>
<td>20</td>
<td>118.8</td>
<td>68.2</td>
<td>3</td>
</tr>
<tr>
<td>Ni-Co-P-300</td>
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<td>150</td>
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<td>Ni$_3$P/CNT</td>
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<td>124</td>
<td>41</td>
<td>5</td>
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<td>Ni$_3$P$_4$ solid NPs</td>
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<td>6</td>
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<td>Ni$_3$P/NRGO</td>
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<td>7</td>
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<td>Ni$_3$P/CNSs-20</td>
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<td>8</td>
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<tr>
<td>Ni$_3$P</td>
<td>20</td>
<td>130</td>
<td>46</td>
<td>9</td>
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