Three-dimensional amorphous tungsten-doped nickel phosphide microsphere as an efficient electrocatalyst for hydrogen evolution

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9. The polarization curves with different W content;
10. The polarization curves of a-WNP with different mass loading;
11. Study of the HER activity for a-WNP in basic electrolyte;
12. Nyquist plots for the a-WNP modified electrodes with Nafion, PVDF as binder and binder-free method;
13. SEM images of WNPTF;
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Fig. S1. XRD pattern of a-WNP. A typical wide peak is exhibited assigned to the amorphous structure of a-WNP.
Fig. S2. High resolution XPS spectrums of Ni 2p, P 2p and W 4f.
The onset-potential for HER was obtained from Tafel plot. For example, the semi-log plot of a-WNP in the region of low current densities as shown in Fig. S3 shows a linear relationship below -51 mV but starts to deviate above -49 mV. Therefore, -50 mV was chosen as the onset potential for a-WNP. The same method was applied on determining the overpotential for other samples in the paper.

Fig. S3. The Tafel plot of a-WNP in the region of low current density.
**Table S1.** A summarized comparison of some reported HER catalysts and a-WNP in acidic electrolyte.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>η(mV)@5 mA cm⁻²</th>
<th>η(mV)@20 mA cm⁻²</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₂P</td>
<td>110</td>
<td>130</td>
<td>46</td>
<td>2</td>
</tr>
<tr>
<td>MoS₂/rGO</td>
<td>130</td>
<td>170</td>
<td>41</td>
<td>3</td>
</tr>
<tr>
<td>Ni/NiO/CoSe₂ nanocomposite</td>
<td>90</td>
<td>140</td>
<td>39</td>
<td>4</td>
</tr>
<tr>
<td>defect-rich MoS₂ nanosheets</td>
<td>170</td>
<td>210</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>WS₂/rGO</td>
<td>240</td>
<td>280</td>
<td>58</td>
<td>6</td>
</tr>
<tr>
<td>MoP network</td>
<td>110</td>
<td>150</td>
<td>54</td>
<td>7</td>
</tr>
<tr>
<td>MoSₓ/graphene/Ni foam</td>
<td>120</td>
<td>160</td>
<td>43</td>
<td>8</td>
</tr>
<tr>
<td>MoP</td>
<td>125</td>
<td>160</td>
<td>53</td>
<td>9</td>
</tr>
<tr>
<td>a-WNP</td>
<td>75</td>
<td>110</td>
<td>39</td>
<td><strong>This work</strong></td>
</tr>
</tbody>
</table>

This work
Determine of the turnover frequency (TOF):

The number of active sites was firstly taken into account and obtained as follow: CV measurements were carried out in neutral PBS solution (pH = 7). Then, the absolute components of the voltammetric charges (cathodic and anodic) reported during one single blank measurement was 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 \( (n) \) of the a-WNP electrode.

The TOF(s\(^{-1}\)) was calculated following equation:

\[
\text{TOF} = \frac{I}{2nF}
\]

where \( I \) is the current (A) during the LSV measurement in 0.5 M H\(_2\)SO\(_4\), \( F \) is Faraday constant (96485 C mol\(^{-1}\)) and \( n \) is the number of active sites (mol). The factor 1/2 arrives by taking into account that two electrons are required to form one hydrogen molecule from two protons.\(^{10,11}\)
The electrochemical active surface area (EASA) was calculated according to the 
electrochemical double-layer capacitance with a blank glassy carbon electrode (GCE) 
as reference. EASA of GCE was obtained using the following equation: 12

\[ i_p = 0.4463 \times 10^{-3} \times n^{3/2} \times F^{3/2} \times A \times C_R^* \times D^{1/2} \times v^{1/2} \times (RT)^{-1/2} \]

where \( n \) is the number of electrons transferred (ferrocyanide, \( n=1 \)), \( F \) is Faraday’s 
constant (96485 C mol\(^{-1}\)), \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the 
temperature (298 K), \( C_R^* \) (mol L\(^{-1}\)) is the initial ferrocyanide concentration, and \( v \) is 
the CV scan rate (0.05 V s\(^{-1}\)). The diffusion coefficient (\( D_R \)) of ferrocyanide was 
based on reference data\(^{12} \) (3.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}), and the calculated EASA of the GCE 
was 0.2 cm\(^2\).

The EASA of the porous N/C electrodes was calculated using a double-layer 
capacitor in Fig. S4 and the following equation: 13

\[ C = A \times (\varepsilon_r \times \varepsilon_0) / d = (\int I \times dV) / v \times m \times V \]

where \( \varepsilon_r \) is the electrolyte dielectric constant, \( \varepsilon_0 \) is the dielectric constant of the 
vacuum, \( d \) is the effective thickness of the double layer (charge separation distance), 
\( A \) is the EASA, \( I \) is the response current density, \( V \) is the potential (V), \( v \) is the 
potential scan rate, and \( m \) is the mass of the catalyst in the electrodes. The EASA of 
Ni\(_x\)P based electrode can be calculated using the equation: \( A_1/A_2=C_1/C_2 \) (\( A_1 \) is EASA 
of glassy carbon electrode, and \( A_2 \) is EASA of the catalyst modified electrode). The 
results are summarized in Table S2.
**Fig. S4.** cyclic voltammograms of above catalysts at different scan rates of 2, 10, 50, 100 and 200 mV s\(^{-1}\) in 0.1 M KOH.
Table S2. Calculated EASA of the four catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>EASA (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WNPTF</td>
<td>9</td>
</tr>
<tr>
<td>a-NP</td>
<td>17</td>
</tr>
<tr>
<td>c-WNP-400</td>
<td>13.5</td>
</tr>
<tr>
<td>a-WNP</td>
<td>15</td>
</tr>
</tbody>
</table>
Fig. S5. Polarization curves of the catalysts in 0.5 M H₂SO₄; the current densities are normalized by the mass loading.
Fig. S6. Steady-state chronoamperometric curve of a-WNP and a-NP for 10000 s at an applied potential of - 0.1 V vs. RHE in 0.5 M H₂SO₄.
Fig. S7. An optical photograph of the collected H$_2$SO$_4$ electrolyte after sweeping between -0.2 V to +0.2 V for 1000 cycles by using the above three electrode as anode.
Fig. S7. Polarization curves of the a-WNP in different content of W.
Fig. S8. Polarization curves of the a-WNP deposited for different length of time, the current densities are normalized by the geometrical area.
Fig. S9. CVs of the a-WNP deposited on Ni foam for 3, 10 and 15 min in 0.1 M KOH with a scan rate of 100 mV s\(^{-1}\). The decrease of electrochemical double-layer charged current density with the extend of the reaction time indicates a decline of EASA.
Fig. S10. Polarization curves of the Ni foam, WNPTF, a-NP, c-WNP-400, a-WNP and Pt/C catalysts in 1.0 M KOH.
Fig. S11. Tafel plot of a-WNP in 1.0 M KOH.
**Table S3.** Comparison of HER performance in alkaline media for a-WNP with other HER electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\eta$(mV)@5 mA cm$^{-2}$</th>
<th>$\eta$(mV)@20 mA cm$^{-2}$</th>
<th>Tafel slope(mV dec$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$_2$C</td>
<td>170</td>
<td>210</td>
<td>54</td>
<td>14</td>
</tr>
<tr>
<td>MoB</td>
<td>210</td>
<td>240</td>
<td>59</td>
<td>14</td>
</tr>
<tr>
<td>Ni$_2$P</td>
<td>150</td>
<td>200</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Co$_2$P</td>
<td>200</td>
<td>250</td>
<td>129</td>
<td>10</td>
</tr>
<tr>
<td>a-WNP</td>
<td>110</td>
<td>180</td>
<td>98</td>
<td>this work</td>
</tr>
</tbody>
</table>
Fig. S11. Steady-state chronoamperometric curve of a-WNP and a-NP for 10000 s at an applied potential of -0.1 V vs. RHE in 1.0 M KOH.
Fig. S12. EIS spectra of the a-WNP modified electrode with the binder of Nafion, PVDF and binder-free direct deposit at the overpotential of 0.2 V.
Fig. S13. SEM image of WNPTF on Ni foam. The dense films could be observed which lead to the decrease of specific area and less active sites exposed to catalyze hydrogen generation.
References: