This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
FeP and FeP_2 Nanowires for Efficient Electrocatalytic Hydrogen Evolution Reaction†

Chang Yong Son, In Hye Kwak, Young Rok Lim and Jeunghee Park*

We report achieving efficient electrocatalytic hydrogen evolution reaction using composition-controlled iron phosphide (FeP and FeP_2) nanowires. The respective Tafel slopes of nanowire arrays were 39 and 37 mV dec^{-1} in 0.5 M H_2SO_4, and 75 and 67 mV dec^{-1} in 1 M KOH. The richer P composition produced excellent electrocatalytic efficiency.

Hydrogen generated from water splitting has great potential for use as a clean, recyclable, and relatively low-cost energy source. Over the past decade, fundamental progress has been made in developing novel catalyst materials for water-splitting reactions. However, constructing an efficient device capable of producing hydrogen at a scale and cost that can compete with fossil fuels remains a significant challenge. Currently, platinum (Pt) is state-of-art catalyst as only small overpotentials are required for high reaction rates. However, the scarcity and high cost of Pt may limit its widespread technological use. This limitation has motivated significant efforts toward replacing Pt with earth-abundant non-noble metal or metal-free materials. Transition metal phosphides are one type of attractive semiconductor materials, which have a low band gap, making them electrically conductive, and exhibit good stability in acidic and basic media compared to their pure metal counterparts.

Despite the remarkable hydrogen evolution reaction (HER) activity of metal phosphides used in water splitting, controlling the composition of these materials to increase their efficiency remains challenging, and only a few cases have been reported. Recently, Schaak’s group reported that CoP exhibits better HER catalytic activity than CoP. Additionally, a number of works have confirmed the higher HER efficiency of P-rich Ni_5P_4 nanostructures and the lower efficiency of P-deficient Ni_3P_4 compared to Ni_3P. Motivated by these results, herein, we developed novel synthetic methods to produce FeP and FeP_2 nanowires (NWs) with two different morphologies; one is NW array directly grown on substrates and the other one is freestanding NWs. We demonstrated the relatively high electrocatalytic activity of P-rich FeP_2 NWs for HER in both acidic and basic media.

FeP and FeP_2 NW arrays were synthesized through the phosphidation reaction of pre-grown vertically aligned Fe_2O_3 NWs with phosphine (PH_3) gas. This method has many advantages, including high yield, short reaction time, and excellent reproducibility and requires no additional fabrication processes. The detailed experimental procedure is described in the Electronic Supplementary Information (ESI†).

---

Fig. 1 SEM micrographs of (a) Fe_2O_3 and (b) FeP_2 NW arrays grown on substrates. Photographs show a red Fe_2O_3, a black FeP, and a grey FeP_2 NW arrays on a 1×1 cm^2 size Fe foil. HRTEM and corresponding FFT images of orthorhombic-phase (c) FeP and (d) FeP_2 NWs. EDX mapping and line-scan profiles of Fe K shell, P K shell, and O K shell showing the Fe_2O_4-FeP and Fe_3O_4-FeP_2 core-shell structures.

Fig. 1a presents the SEM image of the vertically aligned Fe_2O_3 NWs. The photograph shows the homogenous growth of Fe_2O_3 NWs (red) over a large area of substrate (1×1 cm^2). These NWs were synthesized by oxidizing Fe foil, as described elsewhere. The average length of these NWs is 10 μm. After the phosphidation reaction, red color (Fe_2O_3) becomes black (FeP) or grey (FeP_2). The
SEM images and photographs show the homogenous growth of FeP and FeP$_2$ NWs over entire substrates (Fig. 1b). Control over the composition was achieved by varying the reaction temperature; 350 °C for FeP and 400 °C for FeP$_2$. X-ray diffraction (XRD) pattern analysis confirmed the orthorhombic phase of the FeP (JCPDS No. 78-1443, $\alpha = 5.193$ Å, $b = 3.099$ Å, $c = 5.792$ Å) and FeP$_2$ (JCPDS No. 71-2234, $\alpha = 4.972$ Å, $b = 5.656$ Å, $c = 2.723$ Å) NWs (see the ESI†, Fig. S1). Both samples contain the Fe$_2$O$_3$ phase, which was probably produced by the reduction of Fe$_2$O$_3$ under hydrogen-rich condition during the phosphidation reaction. We separated the Fe$_2$O$_3$ NW array by the thermal reaction of as-grown Fe$_2$O$_3$ at 650 °C using hydrogen gas. The density of the as-grown FeP and FeP$_2$ NWs is measured to be ca. 60 and 45 mg cm$^{-2}$, respectively.

Fig. 1c presents the high-resolution transmission electron microscopy (HRTEM) and fast-Fourier transform (FFT) images of the FeP NWs. The average diameter is 250 nm. A rough surface was observed along the entire wire axis of the FeP NWs. The NW’s edge is measured to be ca. 60 and 45 mg cm$^{-2}$, respectively.

Fig. 1d presents the high-resolution transmission electron microscopy image and FFT images of the FeP NWs. The average diameter is 300 nm. Magnifying the image reveals the surface’s polycrystalline nature. The d-spacing between the neighboring (111) planes (d$_{111}$) is 2.4 Å (at the zone axis of [123]), which is consistent with that of orthorhombic-phase FeP. Energy-dispersive X-ray fluorescence (EDX) mapping and the line-scan profile of Fe K shell, P K shell, and O K shell show that the atomic ratio of Fe and P is 1:1 in the outer region and that the oxygen is mainly distributed inside the NWs, suggesting a Fe$_2$O$_3$-Fe$_2$P core-shell structure.

The HRTEM and FFT images of the FeP$_2$ NWs are shown in Fig. 1d. The average diameter is 300 nm. Magnifying the image reveals the surface’s polycrystalline nature. The d-spacing between the neighboring (200) planes (d$_{200}$) is 2.5 Å at the zone axis of [010], which is consistent with that of orthorhombic-phase FeP$_2$. EDX mapping and line-scan profiles reveal the Fe$_2$O$_3$ phase in the cores of the FeP$_2$ NWs. The Fe and P exist at an atomic ratio of 1:2 in the shell part of Fe$_2$O$_3$-FeP$_2$ core-shell structures.

To evaluate the electrocatalytic HER performance, we performed linear sweep voltammetry (LSV) using the as-grown NW arrays as the working electrode. A typical three-electrode setup was used (see the ESI† for experimental details). Table 1 summarizes the results.

Fig. 2a shows the LSV curves (with iR-corrected) for FeP and FeP$_2$ NWs in $\text{H}_2$-saturated 0.5 M $\text{H}_2\text{SO}_4$ solution (scan rate: 2 mV s$^{-1}$). The potentials reported here were referenced to the reversible hydrogen electrode (RHE) through standard calibration. The overpotential ($\eta$) is defined as the applied potential (E) vs. RHE. For reference, we also performed measurements using a commercial Pt/C catalyst (20 wt % Pt on Vulcan carbon black), exhibiting high HER catalytic performance (with a near-zero overpotential). The Pt/C (1 mg cm$^{-2}$) was deposited on a glassy carbon (GC) electrode, and the performance was examined at a rotation speed of 1600 rpm. The LSV curves of Fe$_2$O$_3$ and Fe$_2$O$_3$ NW array were measured, confirming no HER catalytic activity. The overpotentials needed to deliver 10 mA cm$^{-2}$ current density were found to be 96, 61, and 15 mV for FeP, FeP$_2$, and Pt/C, respectively.

The catalysis kinetics for the HER was examined using Tafel plots based on the Tafel equation: $\eta = b \log(\text{J}/\text{J}_0)$ (Fig. 2b). The Tafel slope ($b$) and exchange current density ($J_0$) were obtained from the linear portion in the low-potential region, which corresponds to the activation-controlled current density region. The Tafel slopes are 39, 37, and 30 mV dec$^{-1}$ (dec = decade) for FeP, FeP$_2$, and Pt/C, respectively. The respective exchange currents are 0.17, 0.55, and 3.23 mA cm$^{-2}$. The results confirm the higher catalytic activity of FeP$_2$ relative to FeP, which is consistent with the results obtained for CoP, CoP$_2$, Ni$_3$P$_2$, Ni$_3$P, and Ni$_3$P$_2$.27-31

**Table 1** Experimental overpotential and Tafel plot parameters of FeP and FeP$_2$ NWs

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Sample</th>
<th>$\eta$ (mV)</th>
<th>$b$ (mV dec$^{-1}$)</th>
<th>$J_0$ (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 M $\text{H}_2\text{SO}_4$</td>
<td>FeP array</td>
<td>96</td>
<td>39</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>FeP$_2$ array</td>
<td>61</td>
<td>37</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>FeP free</td>
<td>193</td>
<td>66</td>
<td>0.039</td>
</tr>
<tr>
<td></td>
<td>FeP$_2$ free</td>
<td>128</td>
<td>40</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Pt/C</td>
<td>15</td>
<td>30</td>
<td>3.23</td>
</tr>
<tr>
<td>Base:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 M KOH</td>
<td>FeP array</td>
<td>194</td>
<td>75</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>FeP$_2$ array</td>
<td>189</td>
<td>67</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>FeP free</td>
<td>274</td>
<td>134</td>
<td>0.095</td>
</tr>
<tr>
<td></td>
<td>FeP$_2$ free</td>
<td>253</td>
<td>100</td>
<td>0.032</td>
</tr>
<tr>
<td></td>
<td>Pt/C</td>
<td>90</td>
<td>53</td>
<td>0.87</td>
</tr>
</tbody>
</table>

$a$ Overpotential at $i=10$ mA cm$^{-2}$  
$b$ Parameters of the Tafel equation: $\eta = b \log(J/J_0)$, where $\eta$ is the overpotential (measured), $b$ is the Tafel slope (mV dec$^{-1}$), $J$ is the current density (measured), and $J_0$ is the exchange current density (mA cm$^{-2}$).

d Freestanding NWs.

The Tafel slope of 30 mV dec$^{-1}$ for Pt/C indicates that the HER follows the Volmer-Tafel mechanism; $\text{H}_2\text{O} + e^- \rightarrow \text{H}_2\text{ads}$ and $\text{H}_2\text{ads} \rightarrow \text{H}_2$ ($b = 30$ mV dec$^{-1}$). For FeP and FeP$_2$ NWs, the Volmer-Heyrovsky mechanism; $\text{H}_2\text{O} + e^- \rightarrow \text{H}_2\text{ads} + \text{H}_2\text{ads}$ and $\text{H}_2\text{ads} + \text{H}_2\text{ads} \rightarrow \text{H}_2 + \text{H}_2$ ($b = 40$ mV dec$^{-1}$), is at work. The Tafel slope determined here is near the lowest value reported previously: 32 mV dec$^{-1}$ measured for FeP nanoparticles on carbon cloth in 0.5 M $\text{H}_2\text{SO}_4$ by Sun’s group.15 Table S1 (see the ESI†) summarizes the previous works investigating FeP and FeP$_2$.

The electrocatalytic HER performance was also measured in 1 M...
KOH, as shown in Fig. 2c. The overpotentials needed to deliver $J = 10\, \text{mA cm}^{-2}$ were found to be 194, 189, and 90 mV for FeP, FeP$_2$, and Pt/C, respectively. Correcting the raw data for iR losses revealed even more impressive performance of FeP$_2$ compared to that of FeP. The linear portions of the Tafel plots were fit to the Tafel equation, yielding Tafel slopes of 75, 67, and 53 mV dec$^{-1}$ for FeP, FeP$_2$, and Pt/C, respectively (Fig. 2d). The slope values suggest that the HER follows the Volmer-Heyrovsky mechanism. The Tafel slopes are comparable to that reported for FeP nanotubes on carbon cloth: $b = 59.5\, \text{mV dec}^{-1}$.

The chronoamperometric response measurements confirm these materials’ higher stability in base than in acid (see the ESI†, Fig. S2). The FeP NWs are more stable than the FeP NWs, and current attenuations of 20 % and 12 % (at -0.2 V) within 8 h were observed in 1 M KOH for the FeP and FeP$_2$ NWs, respectively. X-ray photoelectron spectroscopy (XPS) data revealed the negligible degradation of FeP NW during HER in 1 M KOH (Fig. S3, ESI†). The SEM images and XRD pattern confirmed that the morphology and phase of FeP NWs are nearly unchanged. It suggests that the FeP NWs are more competitive with the state-of-the-art HER catalysts than the FeP NWs, especially in basic medium.

Fig. 3 (a) SEM micrographs and (b) HRTEM images of freestanding FeP NWs and (c) FeP$_2$ NWs. (d) EDX spectra of FeP and FeP$_2$ NWs, showing Fe:P= 1:1 and 1:2, respectively.

To support this result, we synthesized freestanding FeP and FeP$_2$ NWs containing no trace of the Fe$_2$O$_3$ phase (see the XRD data in the ESI†, Fig. S1) and examined their electrocatalytic efficiency. The NWs were synthesized via a thermal reaction of pre-grown Fe NWs (synthesized by filament-assisted thermal decomposition of Fe(CO)$_5$ with PH$_3$. SEM image showed a chain-like wire morphology (Fig. 3a). HRTEM and FFT images revealed that the single-crystalline FeP nanocrystals aggregate to form the wire (Fig. 3b). The FeP NWs also have a polycrystalline nature (Fig. 3c). For the single-crystalline domain of FeP and FeP$_2$, $d_{111} = 2.7$ Å (at the zone axis of [211]) and $d_{110} = 3.7$ Å (at the zone axis of [111]) were identified, respectively. The average diameters of FeP and FeP$_2$ NWs are 60 and 100 nm, respectively. EDX spectra show Fe:P= 1:1 and 1:2, respectively, for FeP and FeP$_2$ NWs (Fig. 3d).

The sample (1 mg cm$^{-2}$) was deposited on a GC electrode, and the performance was examined at a rotation speed of 1600 rpm. Table 1 summarizes the current densities (needed to deliver 10 mA cm$^{-2}$) and Tafel parameters. The FeP and FeP$_2$ NWs showed Tafel slopes of 66 and 40 mV dec$^{-1}$ in 0.5 M H$_2$SO$_4$ and 134 and 100 mV dec$^{-1}$ in 1 M KOH, respectively (Fig. S4, ESI†). The current densities are lower than those of the NW arrays. The chronoamperometric response data indicate that the HER catalytic activity of FeP$_2$ is more stable than that of FeP over long-term testing (8 h) in both acidic and basic media (Fig. S5, ESI†). The current attenuation of FeP$_2$ is less than 5 %.

Therefore, we concluded that the richer P composition resulted in persistently excellent electrocatalytic efficiency upon cycling.

We performed XPS measurements to investigate the electronic structures. The peak features are virtually the same for both the array and freestanding NWs (see the ESI†, Fig. S6) and are consistent with previous works. The larger peak shift observed for the FeP NWs is caused by the Fe-P bonding structures. Referring to the data for FeO (Fe$^{2+}$ at 709 eV) and Fe$_2$O$_3$ (Fe$^{3+}$ at 711 eV), the second band is assigned to Fe-O band becomes negligible and the first band is assigned to native (amorphous) oxide layers at the surface, respectively.

The negligible blue shift of the Fe-P bond indicated the metallic state of Fe. For the FeP$_2$ NWs, the Fe-P bond is observed at 707.6 (0.6), which is more blue shifted than that of FeP. This is because of the increased electron withdrawal resulting from the larger amount of P. Nevertheless, the oxidation number of Fe ions in FeP$_2$ would be much less than +2. The Fe-O bond becomes negligible.

Fig. 4b shows the P 2p peaks at 129.5 eV and 129.3 eV for FeP and FeP$_2$ NWs, respectively, which are red shifted by 0.4 and 0.6 eV from the neutral peak (129.9 eV for 2p$_{1/2}$). This band originates from the negatively charged P ions of the P-Fe bonding structures. Referring to the data for FeO (Fe$^{2+}$ at 709 eV) and Fe$_2$O$_3$ (Fe$^{3+}$ at 711 eV), the second band is assigned to native (amorphous) oxide layers at the surface, respectively.

The negligible blue shift of the Fe-P bond indicated the metallic state of Fe. For the FeP$_2$ NWs, the Fe-P bond is observed at 707.6 (0.6), which is more blue shifted than that of FeP. This is because of the increased electron withdrawal resulting from the larger amount of P. Nevertheless, the oxidation number of Fe ions in FeP$_2$ would be much less than +2. The Fe-O bond becomes negligible.

Liu and Rodriguez predicted that Ni$_3$P could be an excellent
catalyst for HER using density functional theory calculations. They suggested that proton-acceptor (P sites) and hydride-acceptor sites (Ni sites) work in a cooperative manner. The same model can be used to rationalize the FeP and FeP$_2$ NWs studied here. Both Fe and P are active sites for the HER, functioning as the hydride-acceptor and proton-acceptor centers, respectively. It was expected that Fe ions in FeP, being more metallic than those in FeP$_2$, became more favorable hydride-acceptor sites. However, more negative charged P anions in FeP$_2$ created the more active proton-acceptor sites. The higher concentration of the exposed active P ions can also increase the catalytic activity. Furthermore the rich P composition protects more effectively the oxidation of metal ions. This probably explains why the FeP$_2$ NWs exhibit higher HER catalytic activity than the FeP NWs with a higher stability.

In summary, we synthesized FeP and FeP$_2$ NW arrays on large substrate areas by reacting pre-grown vertically aligned Fe$_2$O$_3$ NWs (on Fe foils) and PH$_3$. The FeP and FeP$_2$ NWs exhibit excellent performance for electrocatalytic HER in both strong acidic and basic aqueous solutions. The Tafel slopes are 39 and 37 mV dec$^{-1}$ in 0.5 M H$_2$SO$_4$ and 75 and 67 mV dec$^{-1}$ in 1 M KOH, respectively. In addition, we also synthesized freestanding FeP and FeP$_2$ NWs by phosphidation of pre-grown Fe NWs and found that the Tafel slopes are 66 and 40 mV dec$^{-1}$ in 0.5 M H$_2$SO$_4$, respectively. The FeP$_2$ NWs exhibit higher electrocatalytic efficiency and better durability than the FeP NWs. XPS analysis revealed the more negative charged P anions for FeP$_2$, which can create the more active proton-acceptor sites. The richer P composition protects effectively the oxidation of metal ions, which promises a higher stability of catalytic activity. Therefore, the FeP$_2$ NW catalyst that showed excellent performance is a promising material for the development of water-splitting cells able to compete with conventional hydrogen sources.

Notes and references

Entry for the Table of Contents

FeP and FeP$_2$ nanowires exhibit excellent electrocatalytic abilities toward hydrogen evolution from water splitting.