Supporting Information

FeP and FeP₂ Nanowires for Efficient Electrocatalytic Hydrogen Evolution Reaction

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Experimental.

Synthesis of FeP and FeP₂ NW array. As the first step, we synthesized Fe₂O₃ NW arrays as a precursor for iron phosphide NWs. Fe foils were used as both the Fe source and the substrate. A piece of Fe foil $(1 \text{ cm} \times 1 \text{ cm})$ was cleaned with ethanol and placed in a quartz boat inside a quartz tube chemical vapor deposition (CVD) reactor. A mixture of oxygen and argon (Ar) gas with a flow rate of 20 and 200 sccm, respectively, was introduced into the reactor tube, followed by heating to 800 °C. After the oxidation reaction, the Fe₂O₃ NWs were grown on the Fe foil substrates. Next, we placed the asgrown Fe₂O₃ NWs inside the CVD reactor and evacuated it with a mechanical pump, followed by heating to 350-400 °C. Phosphine (PH₃) gas (diluted 20 % by Ar) was introduced into the reactors, which were closed under ambient pressure; the reaction was allowed to proceed for 2 h. Subsequently, the reactors were flushed by flowing N₂ gas at a flow rate of 20 sccm. At 350 °C, the Fe₂O₃ NWs were transformed into Fe₃O₄@FeP core-shell structure NWs. At 400 °C, the Fe₃O₄@FeP₂ core-shell structure NWs were formed. We estimated the mass of NWs grown on the Fe foils using the weight increase (x); $m_{\text{FeP}} = x \times (M_{\text{FeP}}/M_{\text{P}}) = x \times (86.8/31)$ or $m_{\text{FeP2}} = x \times (M_{\text{FeP2}}/M_{\text{P2}}) = x$ \times (117.8/62), where M is the molecular weight or atomic weight. The loading for FeP and FeP₂ NWs was determined to be avg. 60 and 45 mg/cm², respectively, with the use of a high precision microbalance. As reference, the Fe₃O₄ NW array was also

synthesized by placing the as-grown Fe_2O_3 NWs inside the CVD reactor and heating to 650 °C. Pure hydrogen (H₂) gas was introduced into the reactor with a flow rate of 10 sccm for 7 min. After reaction, the reactors were flushed by flowing Ar gas.

Synthesis of freestanding FeP and FeP₂ NWs. A Pyrex reaction chamber was used to generate Fe NWs by thermally decomposing iron pentacarbonyl (Fe(CO)₅) vapor with a resistive heater, as described elsewhere.^{S1} The reaction chamber was evacuated to 10^{-3} Torr, and filled with Fe(CO)₅ vapor to a pressure of 10-30 Torr at room temperature. As the filament was heated by a voltage of 17 V AC, high-purity Fe NWs were uniformly deposited on the reaction chamber wall. These Fe NWs were reacted with PH₃ gas (diluted 20 % by Ar) in a CVD reactor at 350-400 °C, producing the FeP and FeP₂ NWs.

Reference:

(S1) G. H. Lee, S. H. Huh, J. W. Park, H. –C. Ri and J. W. Jeong, Arrays of Ferromagnetic Iron and Cobalt Nanocluster Wires. *J. Phys. Chem. B* 2002, **106**, 2123-2126.

Structural Characterization. The structures and compositions of the products were analyzed by scanning electron microscopy (SEM, Hitachi S-4700), field-emission transmission electron microscopy (TEM, FEI TECNAI G² 200 kV), high voltage TEM (HVEM, Jeol JEM ARM 1300S, 1.25 MV), and energy-dispersive X-ray fluorescence spectroscopy (EDX). High resolution XRD patterns were obtained using the 9B beam lines of the Pohang Light Source (PLS) with monochromatic radiation. XPS data were collected using the 8A1 beam line of the PLS and a laboratory-based spectrometer (Thermo Scientific Theta Probe) with a photon energy of 1486.6 eV (Al K α).

Electrochemical measurements. Electrochemical experiments were performed at room temperature in a three-electrode cell connected to an electrochemical analyzer (CompactStat, Ivium Technologies). A saturated calomel electrode (SCE) or Ag/AgCl electrode was used as the reference electrode, and Pt wire was used as the counter electrode. A 1-cm² piece of NW sample (NW array on Fe foils) was used directly as the working electrode. The edges of the foils were sealed with epoxy resin, and the exposed area was 1 cm². A piece of Cu wire was used to connect the foil with the external circuit through a metal alligator clip. The Pt/C electrodes (as references) were prepared by drop-casting the samples (0.20 mg dispersed in Nafion using isopropyl alcohol) over a glassy carbon electrode (area = 0.1963 cm², Pine Instruments Model No. AFE5T050GC). The freestanding FeP and FeP₂ NW electrodes were prepared by the same method.

All the potentials referred to in this paper are against a reversible hydrogen electrode (RHE). The potential measured against an SCE or Ag/AgCl electrode was converted to the potential versus the RHE according to E (vs. RHE) = E (vs. SCE) + E_{SCE} (= 0.241 V) + 0.0592 pH or E (vs. Ag/AgCl) + $E_{Ag/AgCl}$ (= 0.197 V) + 0.0592 pH. For 0.5 M H₂SO₄ (pH=0), E (vs. RHE) = E (vs. SCE) + 0.241 V. For 1 M KOH (pH=14), E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 V + 0.8288 = E (vs. Ag/AgCl) + 1.0258 V. Calibration of the reference electrode to the reversible hydrogen potential was performed using a Pt disk as a working electrode and a Pt wire as a counter electrode in 0.5 M H₂SO₄. The electrolyte was purged with ultrahigh-purity H₂ gas during the measurement to ensure electrolyte saturation. The electrocatalysis was investigated using linear sweeping from +0.2 to -0.6 V (vs. RHE) with a scan rate of 2-20 mV/s. The overpotential (η) is defined as E (vs. RHE). We performed iR-correction of raw

LSV data for Ohmic losses using the series resistance determined from electrochemical impedance spectroscopy experiments.

Sample Loading ^a	Electrolyte	J (mA cm ⁻²)	η (mV) ^b	Tafel slope (mV dec ⁻¹)	Exchange current (mA cm ⁻²)	References (Corresponding Author) ^c
FeP NPs 0.28 mg/cm ² on GC	$0.5 \text{ M H}_2 \text{SO}_4$	10	~230	67	N/A ^d	[9] Y. Xu et al. Chem. Commun., 2013, 49 , 6656-6658 (B. Zhang)
FeP NPs 1.5 mg/cm ² on C cloth	0.5 M H ₂ SO ₄ PBS (pH=7) 1 M KOH	10 10 10	58 202 218	45 71 146	0.5 N/A N/A	[10] Y. Liang <i>et al. ACS Catal.</i> , 2014, 4 , 4065–4069 (X. Sun)
FeP NPs ~1 mg/cm ² on Ti foil	0.5 M H ₂ SO ₄ 1 M PBS	10 10	50 102	37 N/A	0.43 N/A	[11] J. F. Callejas <i>et al. ACS Nano</i> , 2014, 8 , 11101- 11107 (R. E. Schaak)
FeP NPs (graphene) 0.28 mg/cm ² on GC	$0.5 \ M \ H_2 SO_4$	10	123	50	0.12	[12] Z. Zhang et al. Chem. Commun., 2014, 50 , 11554-1557. (J. Tang)
FeP NW array 3.2 mg/cm ² on Ti foil	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$	10	55	38	0.42	[13] P. Jiang <i>et al. Angew. Chem. Int. Ed.</i> , 2014, 53 , 12855-12859 (X. Sun)
FeP NRs 0.6 mg/cm ² on Ti foil	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$	10	85	60	N/A	[14] R. Liu <i>et al. J. Mater. Chem. A</i> , 2014, 2 , 17263–17267 (C. M. Li)
FeP NPs 4.2 mg/cm ² NPs on C cloth	0.5 M H ₂ SO ₄ 1.0 M PBS	20 20	54 230	32 70	0.59 N/A	[15] J. Tian <i>et al. ACS Appl. Mater. Interfaces</i> , 2014, 6 , 20579–20584 (X. Sun)
$\frac{\text{FeP}_2/\text{C}}{\text{mg/cm}^2 \text{ on GC}} = 0.425$	$0.5 \text{ M H}_2 \text{SO}_4$	10	220	66	1.75×10 ⁻³	[16] J. Jiang <i>et al. J. Mater. Chem. A</i> , 2015, 3 , 449- 503 (Q. Yang)
FeP/C NPs 0.243 mg/cm ² NPs on GC	$0.5 \text{ M H}_2 \text{SO}_4$	10	52	49	N/A	[17] S. Han <i>et al. Adv. Funct. Mater.</i> , 2015, 25 , 3899-3906 (X. Zhuang)
FeP NPs 0.28 mg/cm ² NPs on GC	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$	10	112	58	0.22	[18] Z. Xhang <i>et al. Nanoscale</i> , 2015, 7 , 4400-4405 (J. Tang)
FeP NPs 1.5 mg/cm ² on Ti plate	0.5 M H ₂ SO ₄ 1 M PBS	10 10	116 200	66 99	N/A	[19] Z. Pu et al. Int. J. Hydrogen Energy, 2015, 40 , 5092-5098 (Y. Luo)
FeP NRs 0.2 mg/cm ² on GC	$0.5 \text{ M H}_2 \text{SO}_4$	10	120	55	0.062	[20] H. Du <i>et al. Int. J. Hydrogen Energy</i> , 2015, 40 , 14272-14278 (C. M. Li)
FeP NCs 4.9 mg/cm ² on C cloth	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$	10	34	29.2	0.68	[21] X. Yang <i>et al. Nanoscale</i> , 2015, 7 , 10974- 10981 (L. J. Li)
FeP NTs 1.6 mg/cm ² on C cloth	0.5 M H ₂ SO ₄ 1.0 M KOH	10	88 120	35.5 59.5	N/A	[22] Y. Yam <i>et al. Chem. Eur. J.</i> , 2015, 21 , DOI: 10.1002/chem.201503777 (X. Wang)

Table S1. Comparison of HER electrocatalytic efficiency of FeP and FeP₂ nanostructures

^aNPs = Nanoparticles, NRs = Nanorods, NWs = Nanowires, NTs= Nanotubes, NCs= Nanocrystals, GC = Glassy carbon, C cloth = carbon cloth; ^bOverpotential nee ; ded deliver J =10 mA/cm²; ^cReferences the text; $^{d}N/A$ applicable. to in not =



Figure S1. XRD patterns of Fe₂O₃, Fe₃O₄, FeP, and FeP₂ NW arrays (FeP-A and FeP₂-A), and freestanding FeP and FeP₂ NWs (FeP-F and FeP₂-F). The peaks are indexed using reference peaks; rhombohedral-phase Fe₂O₃ (JCPDS No. 87-1164, RError!c, a = 5.035 Å, c = 13.749 Å), cubic-phase Fe₃O₄ (JCPDS No. 88-0315, FdError!m, a = 8.375 Å), orthorhombic-phase FeP (JCPDS No. 78-1443, Pnma, a = 5.193 Å, b = 3.099 Å, c = 5.792 Å), orthorhombic-phase FeP₂ (JCPDS No. 71-2234, Pnnm, a = 4.972 Å, b = 5.656 Å, c = 2.723 Å),. The peaks of the NW array samples are well matched to those of the FeP and FeP₂ references. Because the probe depth of the XRD exceeds 1 µm, the Fe₃O₄ peaks (marked by *) of NW array sample originated from the Fe₃O₄ core. The freestanding NW peaks are in good agreement with those of the reference. These NW samples show no oxide phase.



Figure S2. Chronoamperometric responses; current density J (mA cm⁻²) vs. time (h), recorded using FeP and FeP₂ NW arrays in 0.5 M H₂SO₄ at a constant applied potential of -0.07 V and in 1 M KOH at a constant applied potential of -0.20 V. In acidic medium, the current densities suddenly decrease within 10 min and 1 h for FeP and FeP₂ NWs, respectively, mainly due to the dissolved Fe foil and the subsequent separation of NW array film from it. In basic medium, the current density degrades by 20 % for FeP NWs and by 12 % for FeP₂ NWs within 8 h, respectively. We conclude that (1) the catalytic activity of FeP₂ NWs is more stable than that of FeP NW and that (2) both FeP and FeP₂ NW arrays are more stable in base than in acid.



Figure S3. Fine-scan XPS Fe $2p_{3/2}$ and $2p_{1/2}$ and P 2p peaks of (a) FeP and (b) FeP₂ NW array before and after 8 h chronoamperometric measurements in 1 M KOH. For FeP₂ NWs, the peak feature remains nearly the same as that of the as-grown FeP₂ NWs In contrast, the intensity of the Fe-P band (at 707 eV) is reduced for FeP NWs, while that of the Fe-O band (at 711 eV) is increased. It concludes that the FeP₂ NWs are more stable as the HER catalysts than the FeP NWs.



Figure S4. (a) LSV (vs. RHE) curves of the HER in 0.5 M H_2SO_4 for freestanding FeP and FeP₂ NWs and corresponding (b) Tafel plots derived from the LSV curves. (c) LSV (vs. RHE) curves of the HER in 1 M KOH for freestanding FeP and FeP₂ NWs and corresponding (d) Tafel plots derived from the LSV curves. The scan rate is 2 mV s⁻¹.



Figure S5. Chronoamperometric response; current density (mA cm⁻²) vs. time (h), recorded using freestanding FeP and FeP₂ NWs in 0.5 M H₂SO₄ and 1 M KOH. The applied potentials are -0.15 and -0.23 V for acidic and basic media, respectively. The current attenuations of FeP₂ NWs are 3.5 % in acid and 5 % in base over 8 h. FeP NWs exhibit more significant degradation than FeP₂ NWs: 39 % in acid and 30 % in base. This result is consistent with that obtained using NW arrays.



Figure S6. (a) Fine-scan XPS Fe $2p_{3/2}$ and $2p_{1/2}$ and (b) P 2*p* peaks of freestanding FeP and FeP₂ NWs. The position of the neural element peak is marked by a dotted line to delineate the peak shift.

The $2p_{3/2}$ peak of FeP consisted of two bands with peak positions of 707.2 (0.2) and 712.5 (5.5) eV. The peaks of neutral Fe at 720.1 and 707.0 eV are indicated. The value in parentheses represents the blue shift of each band. The first band originated from the Fe-P bonding structures, and the second band is assigned to the Fe-O bonding structure. For FeP₂ NWs, the Fe-P band is observed at 707.6 (0.6), which is blue shifted compared to that of FeP. This is caused by the increased electron withdrawal resulting from the larger amount of P.

The P 2*p* peaks at 129.5 eV and 129.3 eV (FeP₂) for FeP and FeP₂ NWs, respectively, are red shifted by 0.4 and 0.6 eV relative to the neutral one (129.9 eV for $2p_{3/2}$). This band is ascribed to the P-Fe bonding structures. The larger peak shift for the FeP₂ NWs is because of the larger amount of P. The peak at 134 eV is assigned to the P-O bonding structure of the oxide form. The FeP₂ NWs exhibit a smaller P-O band than the FeP NWs.