Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Iron Phosphate Hydroxide Hydrate Electrocatalyst: Synergistic Effects of Fe^{2+} and Fe^{3+} for Enhanced Hydrogen Evolution Reaction Stability

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Electrochemical Measurements:

At room temperature in a 1M KOH electrolyte solution, the SP-150 biologic machine was used for all electrochemical experiments. The electrolyte solution was purged with N_2 gas to eliminate any undissolved gases before each electrochemical experiment. Before measuring the OER and HER tests, the electrode was activated using cyclic voltammetry (CV) in a three-electrode setup at a scan rate of 50 mV/s for 200 cycles. The working, counter, and reference electrodes are catalyst-grown NF, graphite rod, and Hg/HgO (1M KOH), respectively. The working electrode's geometrical area was maintained at 1 cm x 1 cm. The linear sweep voltammetry (LSV) of HER was studied at a scan rate of 1 mV/s with 85% iR correction. The observed potentials ($E_{Hg/HgO}$) were converted to reversible hydrogen electrode (E_{RHE}) values using the Nernst Equation (1)

$$\mathbf{E_{RHE} = E_{Hg/HgO} + (0.0591 * pH) + 0.098\ V.} \qquad \mathbf{(1)}$$

the pH value of the 1M KOH electrolyte is 14.

The Tafel slopes were calculated from the LSV using plots of overpotentials (η) vs. log j using Equation (2).

$$\boldsymbol{\eta = b \log j + a} \qquad \mathbf{(2)}$$

where, b is the Tafel slope, j is the current density, and ‘a’ is constant.

The step chronopotentiometry (CP) was performed at various current densities ranging from 10 to 100 mA/cm^2. Electrochemical impedance spectroscopy (EIS) was measured in the frequency ranges of 0.04 Hz to 10 kHz for HER. The EIS curves were fitted with a corresponding equivalent circuit using Z-fit analysis. The electric double-layer capacitance (C_{dl}) was calculated from CV runs in the non-faradic region ranging from -0.3 to -0.6 (V vs. Hg/HgO) at different scan rates ranging from 10 100 mV s^{-1}. The difference in anodic and cathodic current density ($\Delta j = j_a - j_c$)

vs. the scan rate (ν) yields a straight line, and the slope of this straight line gives $2C_{dl}$ value (Equation (3)).

$$\Delta \mathbf{j} = \mathbf{v.2.C_{dl}} \qquad \textbf{(3)}$$

The C_{dl} obtained can be further used to find ECSA, from Equation (4)

$$\mathbf{ECSA} = \frac{\mathbf{C_{dl}}}{\mathbf{C_s}} \qquad \textbf{(4)}$$

C_s was calculated from galvanostatic charging-discharging characteristics (Equation (5)):

$$\mathbf{C_s} = \frac{\mathbf{I\ \Delta t}}{\mathbf{m\ \Delta V}} \qquad \textbf{(5)}$$

Where I – current density (mA cm^{-2}), Δt – discharging time (s), m – mass loading of the catalyst (mg)

ΔV – potential window (V)

The electrochemically exposed active sites were estimated from the CV swept in the non-Faradic region at 50 mV/s in a 1 M KOH electrolyte using Equation (6)

$$\mathbf{C} = \frac{\int \textbf{area of reduction peak/scan rate}}{\textbf{Charge of one electron}} \qquad \textbf{(6)}$$

The turnover frequency (TOF) was calculated from Equation (7)

$$\mathbf{TOF} = j.\frac{N_A}{n.F.C}\, s^{-1} \qquad \textbf{(7)}$$

where, j = Current density (mA cm^{-2})

NA = Avogadro number (6.02214×10^{23} mol^{-1})

F = Faraday’s constant (96485 C mol^{-1})

n = Number of electrons transferred (For HER = 2)

C = Surface concentration of active sites

The electrocatalyst's long-term stability was tested for 80 hours by the CP technique at a high current density of 100 mA cm^{-2}.

Table S1 : Atomic percentage of Fe and P from EDS and Fe3+/Fe2+ ratio of all the samples from the XPS spectra

Samples	**Fe%**	**P%**	**Fe^{3+}/Fe^{2+}**
FPOH-1	10	90	1.12
FPOH-2	20	80	3.30
FPOH-3	25	75	1.36
FPOH-4	40	60	1.24
FPOH-5	54	46	1.6

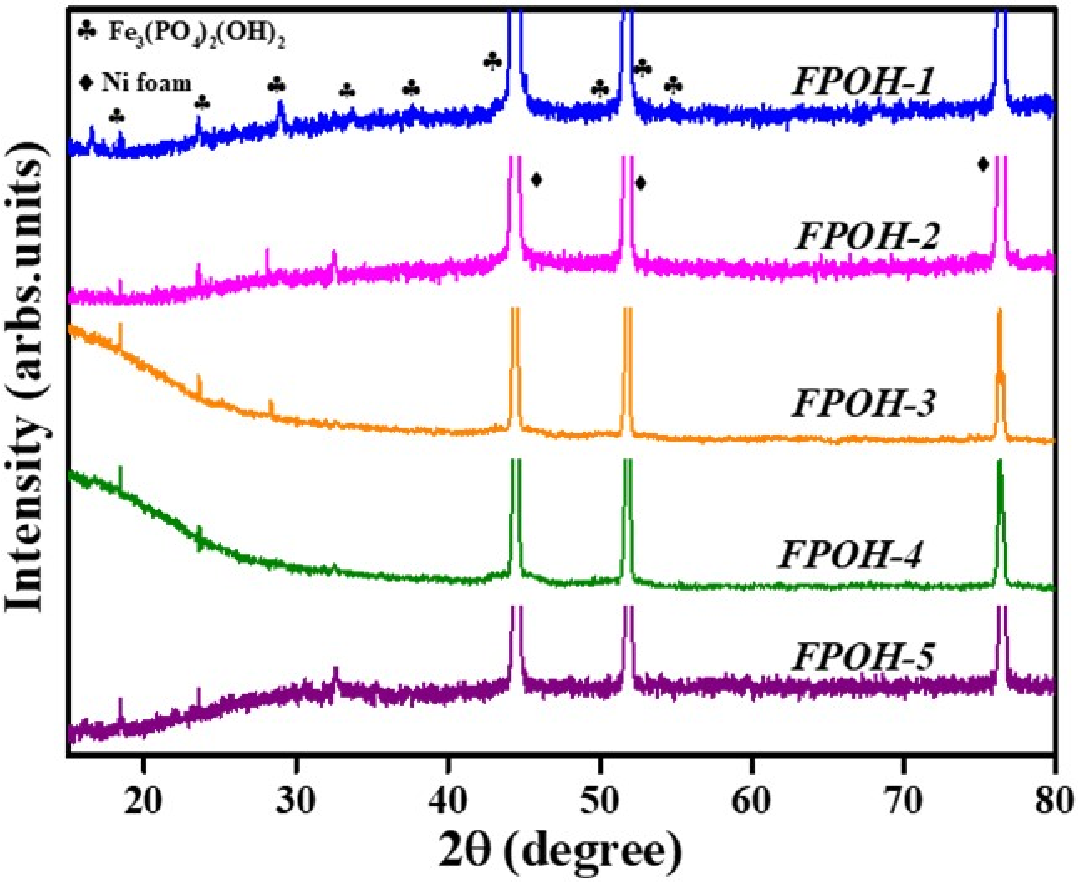


Fig. S1: XRD patterns of as-prepared $Fe_3(PO_4)(OH)_6.3H_2O$

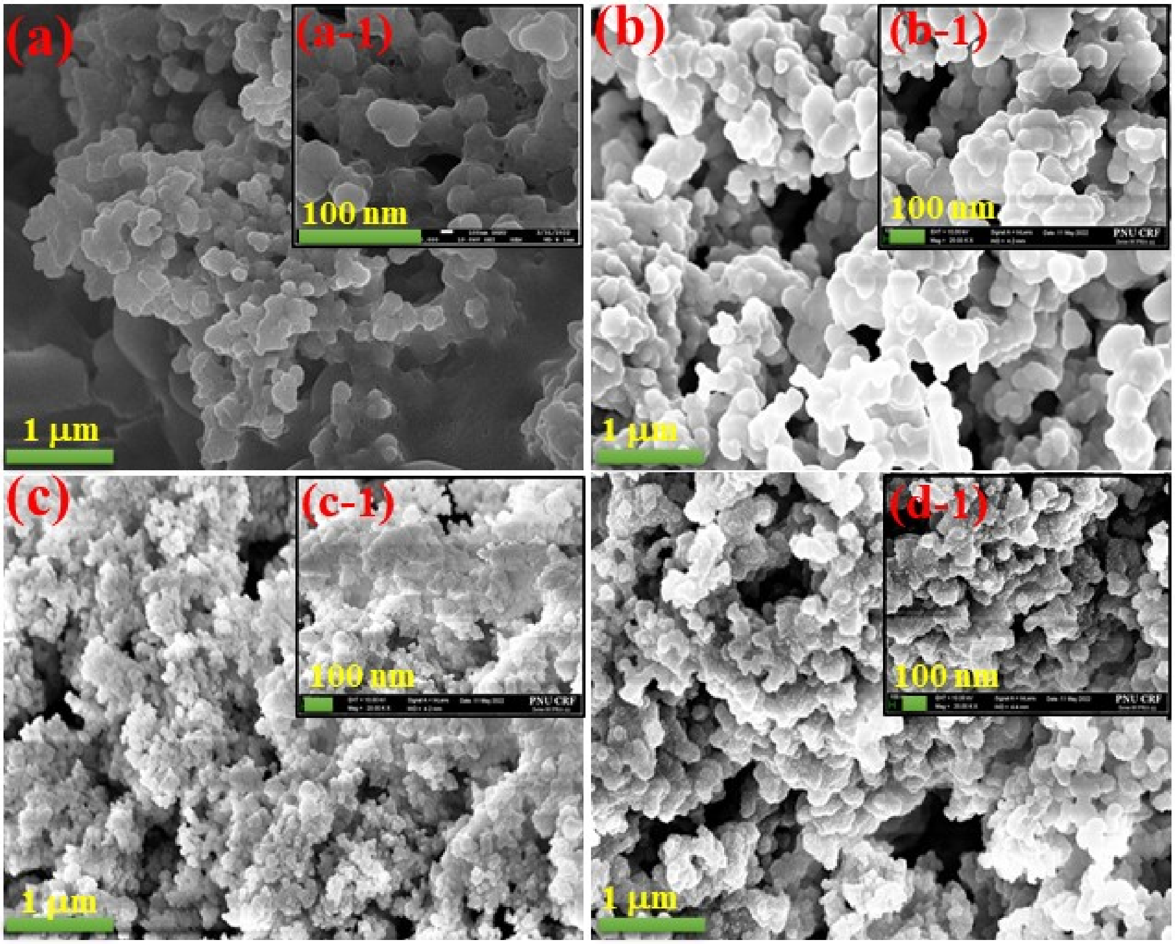
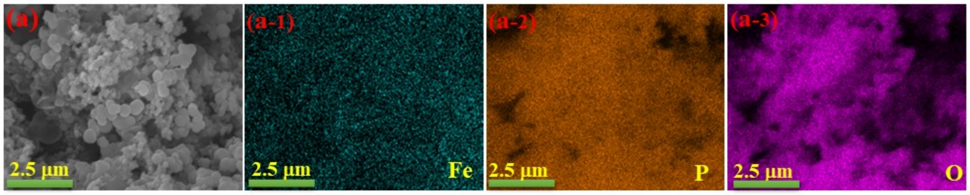
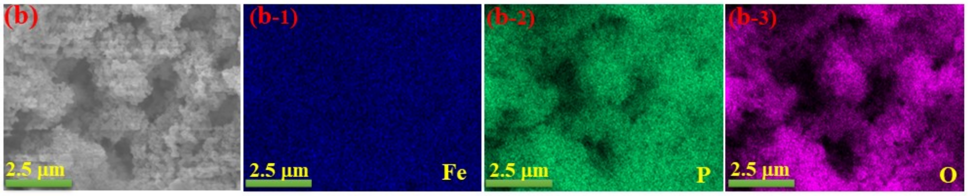


Fig. S2: FE-SEM images of $Fe_3(PO_4)(OH)_6.3H_2O$ (a) FPOH-1, (b) FPOH-3, (c) FPOH- 4, (d)FPOH-5.

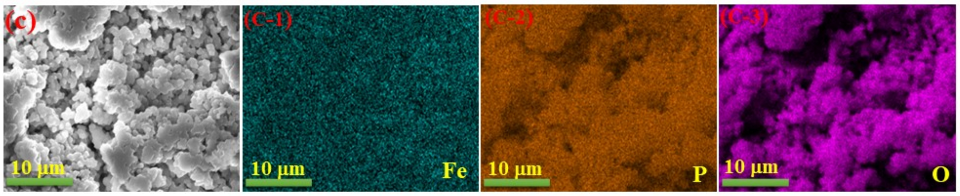
FPOH-1



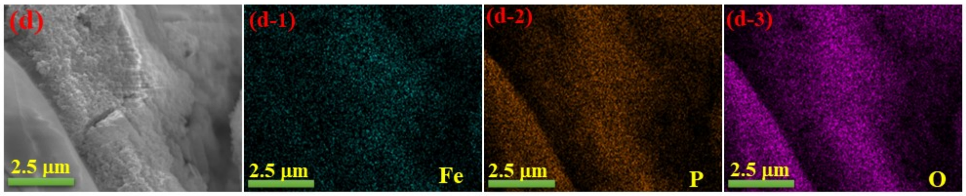
FPOH-2



FPOH-3



FPOH-4



FPOH-5

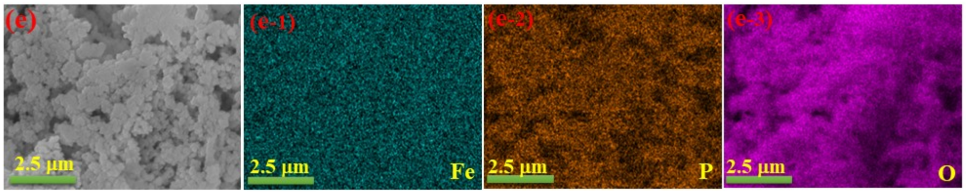


Figure S3: EDAX of the respective samples

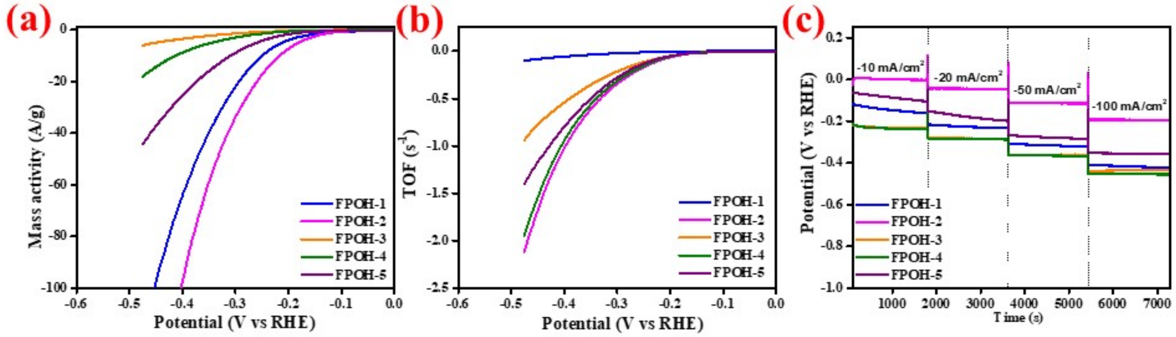


Figure S4: (a) The mass activity, (b) TOF graphs of Iron phosphate hydroxide hydrate, (c) Chronopotentiometry test at different current densities

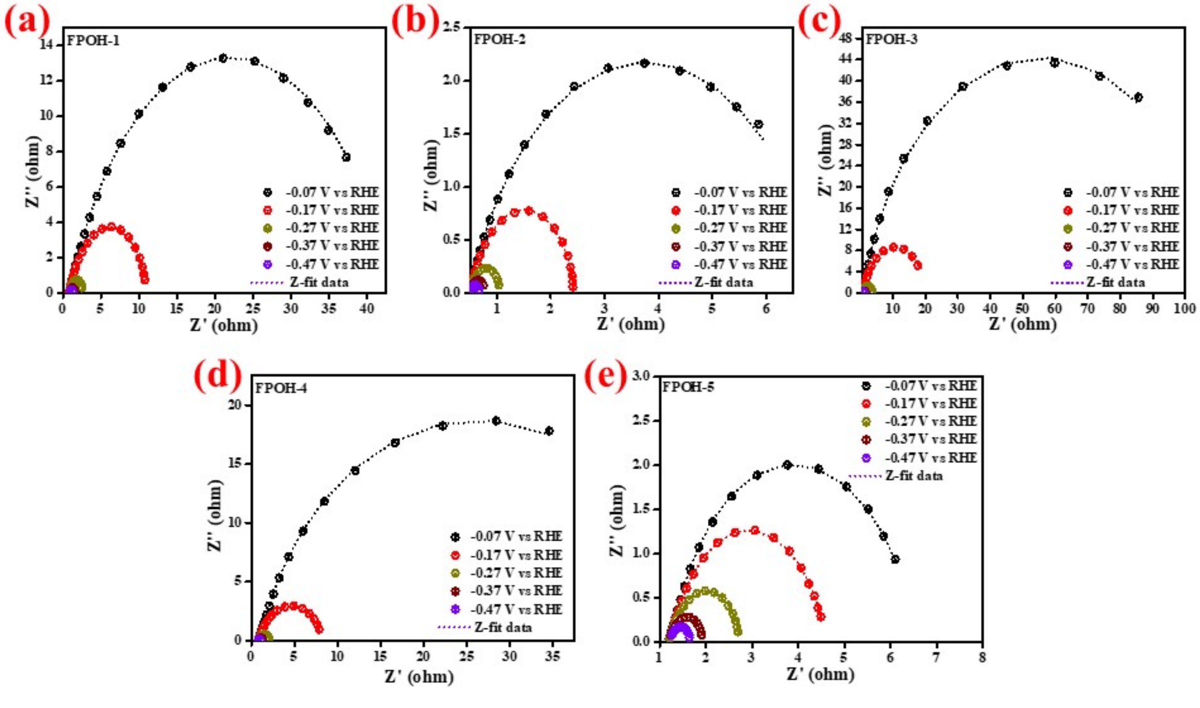


Figure S5: Nyquist plots of samples at different potentials

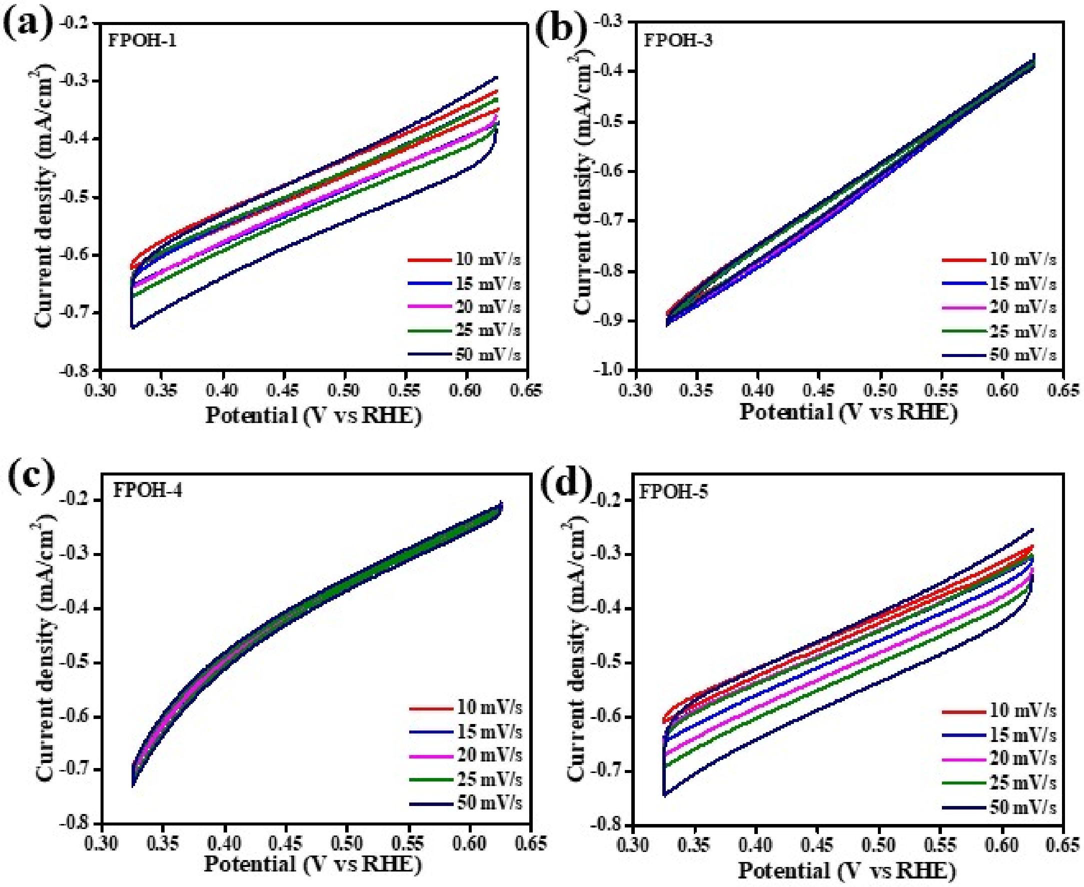


Figure S6: CV curves in non-faradic potential range for the estimation of Cdl

Table S2: Electrochemical active surface area values.

Samples	**C_{dl}** (mF/cm^2)	**C_s** (F/g)	**ECSA** $= \frac{C_{dl}}{C_s}$ (mg/cm^2)
FPOH-1	1.3	0.832	1.59
FPOH-2	425	0.48	885.2
FPOH-3	1.7	0.182	19.0
FPOH-4	0.29	0.43	0.337
FPOH-5	3.2	1.41	1.42

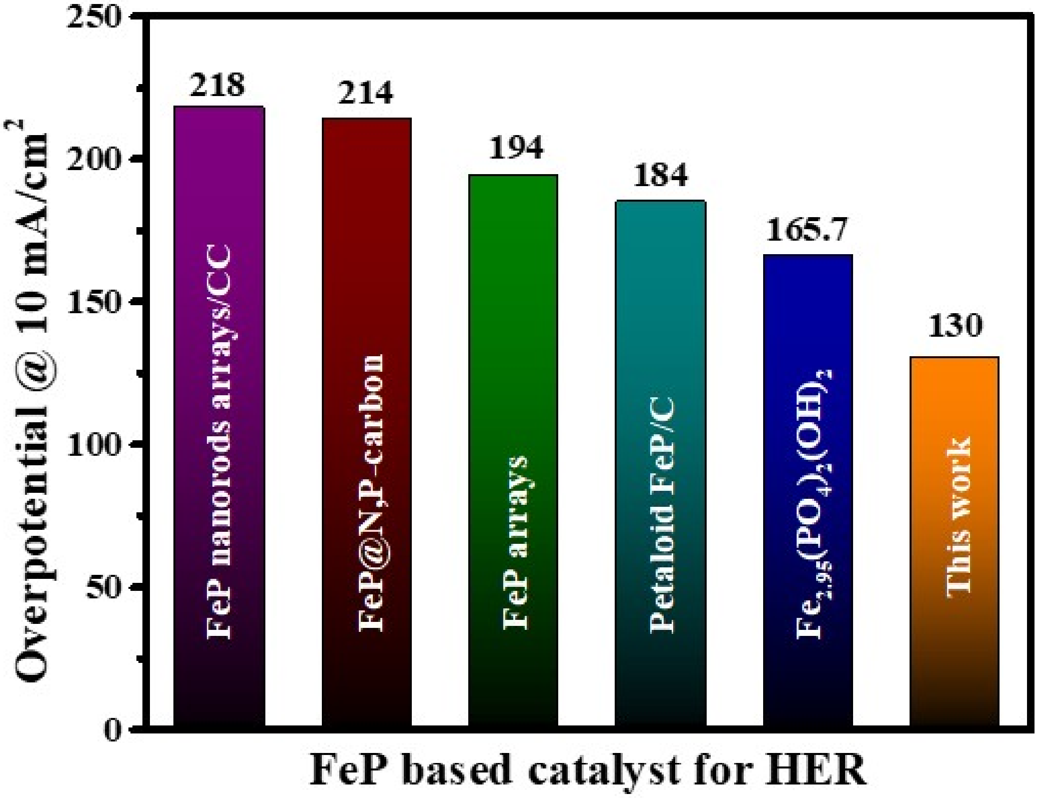


Figure S7: Comparison of Iron phosphate based catalyst for Hydrogen evolution reaction.[1–5]

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