Electronic Supplementary Information (ESI)

Modifying Candle Soot with FeP Nanoparticles as High-Performance and Cost-Effective Catalysts for Electrocatalytic Hydrogen Evolution Reaction

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Experimental Section

Chemicals. Candle was purchased from supermarket. Dimethylformamide (DMF) was purchased from Beijing Chemical Reagent Factory (Beijing, China). Tetraethylene glycol (TEG), NaH_2PO_2, sodium dodecyl sulfate (SDS), and iron (III) acetylacetonate ($Fe(acac)_3$) were purchased from Aladdin Aladdin Industrial Inc. (Shanghai, China). Carbon black (CB, acetylene, 50% compressed) and Platinum on carbon (20% Pt/C, Pt on Vulcan XC-72R carbon support) were purchased Alfa Aesar. All the reagents were used as received without further purification. All aqueous solutions were prepared with Milli-Q water (>18.2MΩ.cm) from a Milli-Q Plus system (Millipore).

Apparatus. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al Kα ($h\upsilon$ = 1486.6 eV) X-ray radiation as the X-ray source for excitation. The energy step size for the binding energy (BE) values was 1 eV and 0.1 eV for survey spectrum and high resolution, respectively. X-ray diffraction (XRD) spectra was obtained on a D8 ADVANCE (Germany) using Cu Kα (1.5406 Å) radiation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a TECNAI G_2 high-resolution transmission electron microscope (Holland) with an accelerating voltage of 200 kV and Hitachi H600 electron microscope (Japan) with an accelerating voltage of 100 kV. The sample for TEM characterization was prepared by placing a drop of prepared solution on carbon-coated copper grid and drying at room temperature. Raman spectra were acquired on a Renishaw (Renishaw, United Kingdom) 2000 model confocal microscopy Raman spectrometer with 514.5 nm wavelength incident laser light. Thermogravimetric analysis (TGA) of sample was performed on a Pyris Diamond TG/DTA thermogravimetric analyzer (Perkin-Elmer Thermal Analysis). Sample was heated under an air atmosphere from room temperature to 800 °C at 10 °C/min. Elemental analysis was performed on a Vario EL cube (Elementar Analysensysteme GmbH) to determine the carbon, nitrogen and hydrogen contents of the samples.

Collection of Candle Soot: Candle soot (CS) was collected by putting a piece of

glass plate on top of burning candles. Glass plate was cleaned by alternate ultrasonication in ethanol and Milli-Q water for three times and then dried in oven. About 5 min after the ignition of the candle, a steady flame was obtained with a total flame height of 4 cm. Afterward, glass plate is held above the flame envelope 3.5 cm above the candle. The growth process lasted for 2 min for one side and then for another 2 min for the other side with glass plate moving back and forth, after which the glass plate was taken out from the flame and candle soot was scratched away with coverslip.

Synthesis of Fe_3O_4-CS and FeP-CS. Fe_3O_4-CS hybrids were synthesized by solvothermal route. In a typical synthesis, 15 mg CS and 50 mg SDS were dispersed into a mixed solution of 10 mL of TEG and 20 mL of DMF by sonication for 30 min. Subsequently, 100 mg of $Fe(acac)_3$ were added to the solution. After sonication for another 30 min, the mixture was transferred to a Teflon-lined stainless steel autoclave for solvothermal reaction at 180 °C for 2 h. After the solvothermal treatment was completed, the autoclave was cooled to room temperature. The final products were collected by centrifugation, washed thoroughly with water and ethanol, and dried at room temperature overnight. The obtained Fe_3O_4-CS hybrids were transferred into a tubular furnace for phosphidation under N_2 flow. 20 mg Fe_3O_4-CS hybrids and 100 mg NaH_2PO_2 were put at two separate positions in a fused silica tube with NaH_2PO_2 at the upstream side of the tubular furnace. Then the Fe_3O_4-GS hybrids were annealed in N_2 up to 350°C for 2 h with a heating rate of 3 °C/min. Black FeP-CS hybrids powders were obtained after cooled to ambient temperature under N_2.

In addition, we further prepared Fe_3O_4 nanoparticles (NPs) and FeP NPs for comparison. Fe_3O_4 NPs were synthesized according to the literature.[1] FeP NPs were obtained similarly by replacing Fe_3O_4-CS hybrids with Fe_3O_4. Fe_3O_4-CB hybrids and FeP-CB hybrids were synthesized similarly by replacing CS with CB.

Electrochemical Measurements: Electrochemical measurements were performed with a CHI 660A electrochemical analyzer (CH Instruments, Inc., Shanghai). Electrochemical properties were studied in a conventional three-electrode system using glassy carbon (Ø 3 mm) modified with the catalysts as the working electrode,

saturated calomel electrode (SCE) as the reference electrode and carbon rod as the counter electrode. The potential, measured against a SCE electrode, was converted to the potential versus the reversible hydrogen electrode (RHE) according to $E_{vs\ RHE} = E_{vs\ SCE} + 0.242 + 0.059pH$. Prior to the experiments, the glassy carbon electrode was polished on a polishing cloth using alumina pastes to obtain a mirror-like surface, followed by ultrasonic cleaning in ethanol and water. To make working electrodes, a stock solution of Fe_3O_4-CS hybrids at 10 mg/mL in water was prepared. 2 μL of this solution was drop-casted onto a GCE, and it was left to dry in air to obtain a catalyst loading of ~0.28 mg/cm^2. 5μL of 0.5% Nafion solution in ethanol was drop-casted on top to protect the film. Before the electrochemical measurement, the electrolyte (0.5 M H_2SO_4, pH=0) was degassed by bubbling argon for 30 min. For Linear Sweep Voltammetry (LSV) measurements, the scan rate was set to be 5 mV/s. To get the Tafel plots, steady-state current density as a function of voltage was measured with a dwell time of 300 s.

For comparison, the electrocatalytic activities of CS, FeP NPs, FeP-CB, and Pt/C were measured under similar conditions.

Electrochemical impedance spectroscopy (EIS) measurements were carried out using a Solartron 1255 B Frequency Response Analyzer (Solartron Inc. UK) in the frequency range of 100 kHz to 100 Hz with excitation amplitude of 10 mV in 0.5 M H_2SO_4.

References

1. L. Xiao, J. Li, D. F. Brougham, E. K. Fox, N. Feliu, A. Bushmelev, A. Schmidt, N. Mertens, F. Kiessling, M. Valldor, B. Fadeel and S. Mathur, *Acs Nano*, 2011, **5**, 6315-6324.

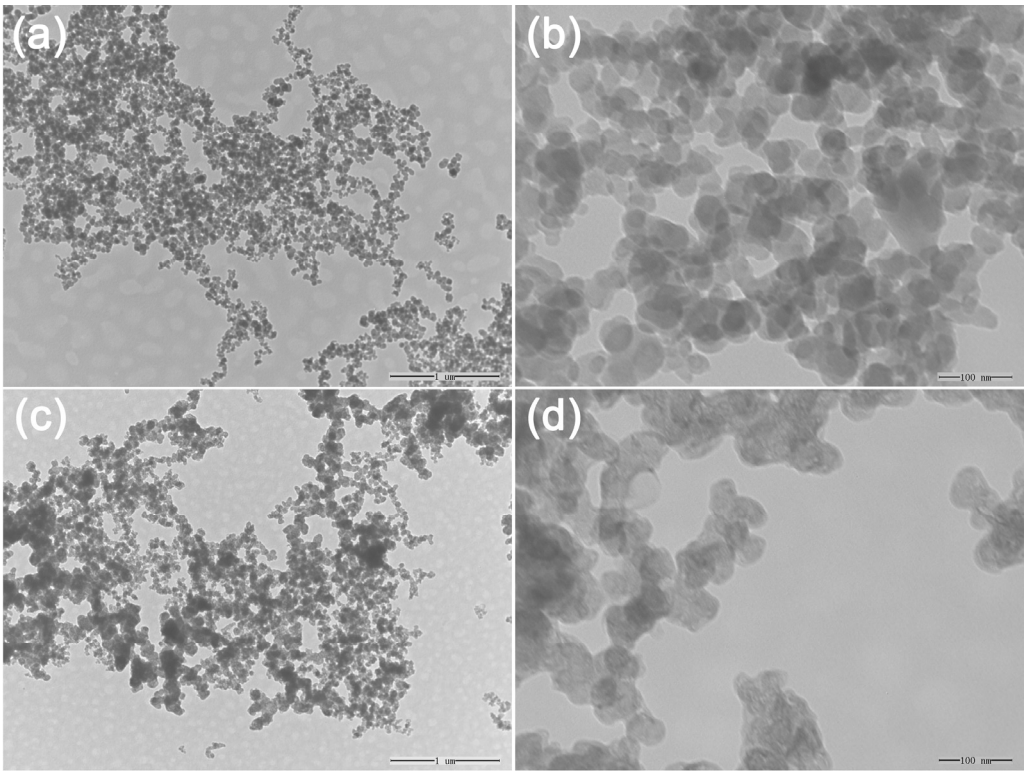

Figure S1. TEM images of CS (a, b) and CB (c, d) at different magnifications.

Table S1. Carbon, nitrogen, and hydrogen contents in the samples obtained from elemental analyzes.

Sample	C (%)	N (%)	H (%)
Candle soot_1	**95.71**	**0.07**	**0.596**
Candle soot_2	**95.75**	**0.09**	**0.513**
Carbon black_1	**99.92**	**0.04**	**0.222**
Carbon black_2	**99.94**	**0.06**	**0.196**

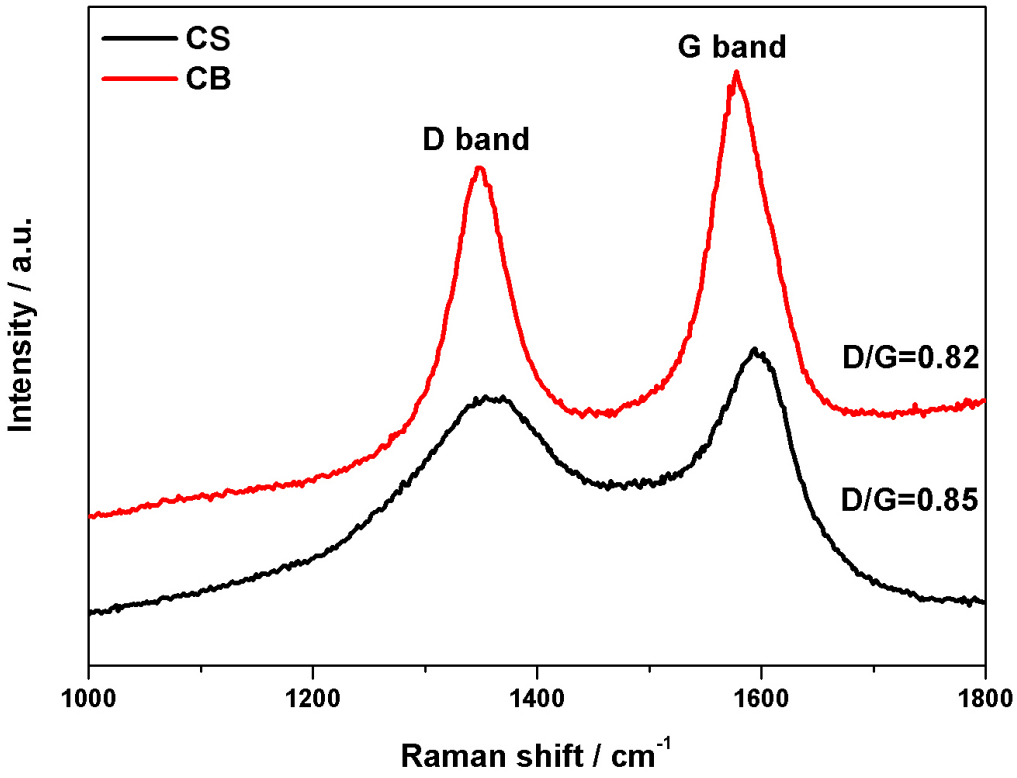

Figure S2. Raman spectra of CS and CB.

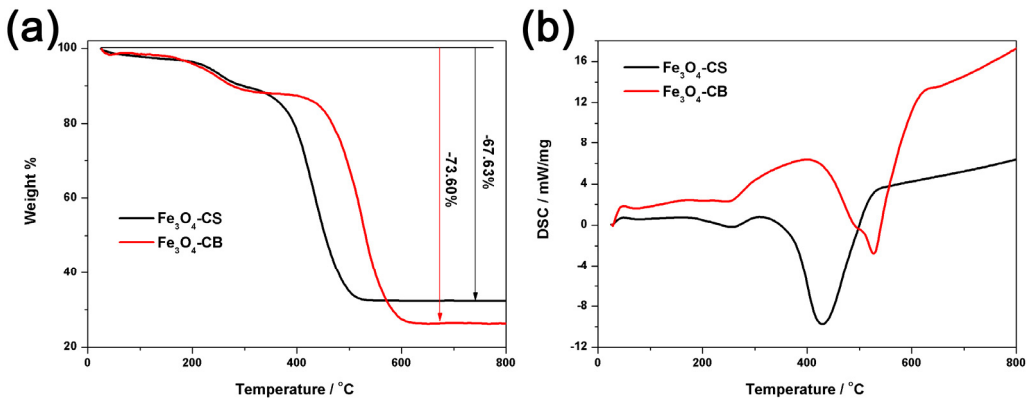

Figure S3. TGA (a) and DSC (b) patterns of Fe_3O_4-CB hybrids and Fe_3O_4-CS hybrids.

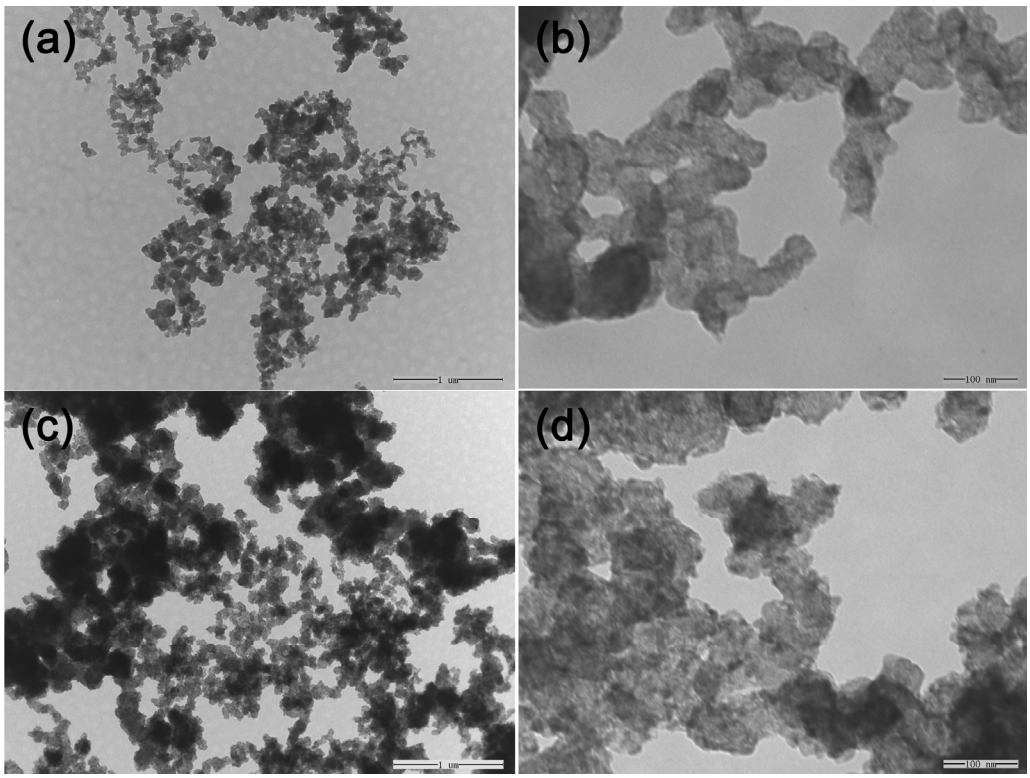

Figure S4. TEM images of Fe_3O_4-CB hybrids (a, b) and FeP-CB hybrids (c, d) at different magnifications.

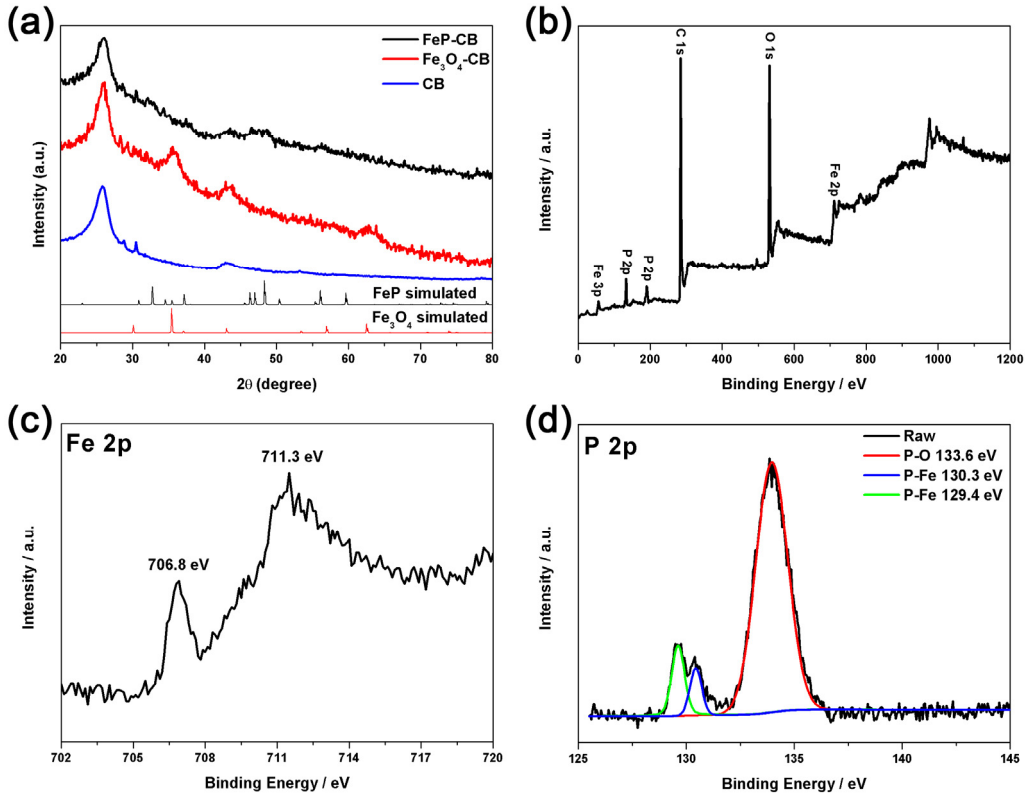

Figure S5. XRD patterns of CB, Fe_3O_4-CB hybrids and FeP-CB hybrids (a). XPS survey spectrum of FeP-CB hybrids (b). XPS spectra in the Fe 2p (c) and P 2p (d) regions for FeP-CB hybrids.

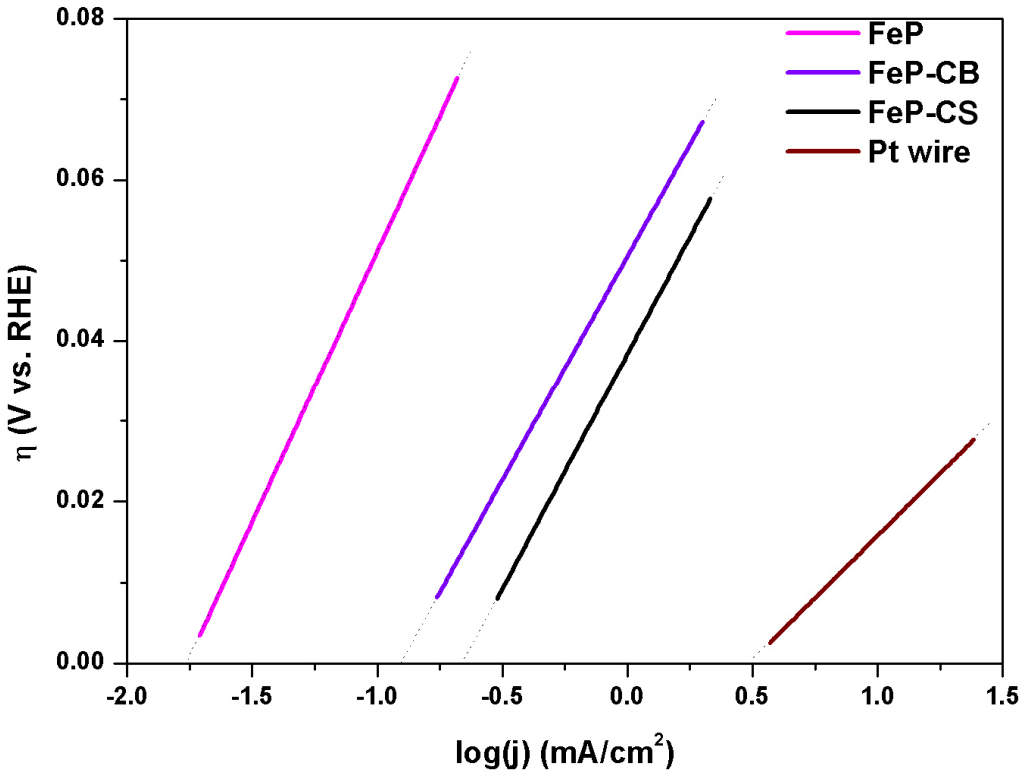

Figure S6. Calculation of exchange current density of FeP, FeP-CB hybrids, FeP-CS hybrids, and Pt wire.

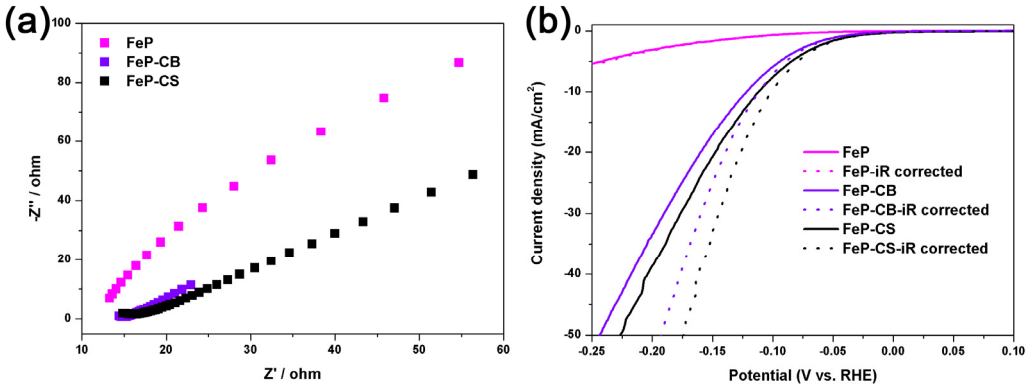

Figure S7. Nyquist plots (a) and linear sweep voltammetry curves (b) of FeP, FeP-CB, and FeP-CS modified electrodes in 0.5 M H_2SO_4 solution.

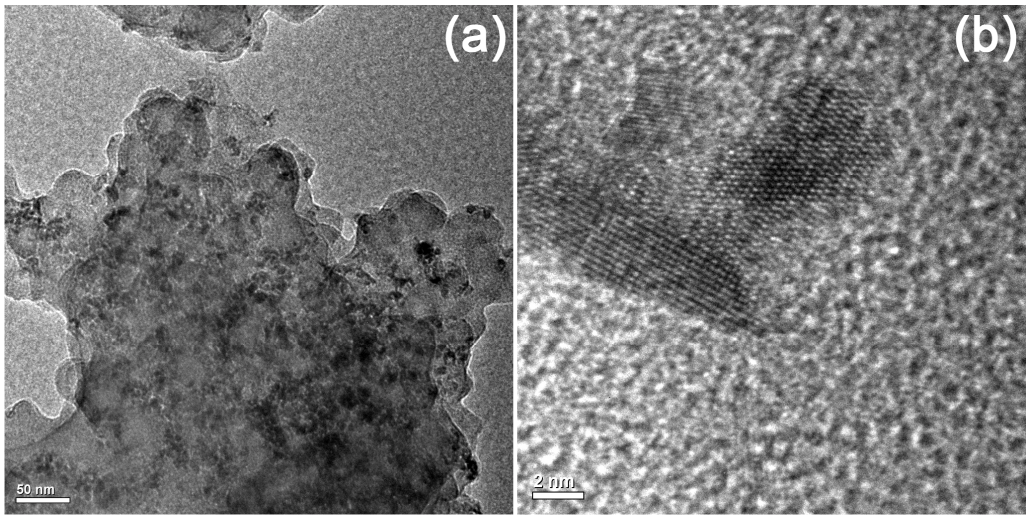

Figure S8. TEM image (a) and HRTEM image (b) of FeP-CS hybrids obtained after under static overpotential of 103 mV for 10 h in 0.5 M H_2SO_4.

Table S2 Comparison of HER performance in 0.5 M H_2SO_4 electrolytes for FeP-CS hybrids with other HER electrocatalysts.

Catalyst	Current density (j, mA/cm^2)	η at the corresponding j (mV)	Exchange current density (mA/cm^2)	Ref.
FeP-CS	10	112	0.22	This work
FeP-GS	10	123	0.12	[30]
FeP nanowire array	10	55	0.42	[15c]
FeP nanosheets	10	~240	--	[15d]
Ni_2P nanoparticles	20	~130	0.033	[16c]
CoP-CNT	10	122	0.13	[24a]
CoP nanoparticles	20	85	0.14	[14a]
CoP nanowire array	10	67	0.288	[14c]
MoS_2/RGO	10	150	--	[28b]
defect-rich MoS_2	13	200	0.00891	[7b]
$NiMoN_x$/C	2	170	0.24	[7c]
MoS_2 film	2	~380	0.0022	[7g]
CoS_2 nanowire	10	145	0.0151	[10]
$Co_{0.6}Mo_{1.4}N_2$	10	200	0.23	[7f]
MoP nanoparticles	10	125	0.086	[17a]
WP nanoparticles	10	120	--	[18]
N-P-graphene	10	420	--	[12b]
WS_2 nanosheets	10	~220	--	[8]