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Electronic Supplementary Information for

In Situ Synthesis of Fe_3S_4/MIL-53(Fe) hybrid catalyst for Efficient Electrocatalytic Hydrogen Evolution

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S1. Experimental section

Materials: All reactants and solvents were purchased and used without purification. Shanghai Mclean company provided ferric chloride hexahydrate ($FeCl_3.6H_2O$), dimethylformamide (DMF), terephthalic acid (1, 4-BDC), dimethylformamide (DMF), ethylene glycol (EG) and Ethanol. Thioacetamide (TAA) was bought from Aladdin Chemicals. Nafion solution (5 wt%) were purchased from Macklin Chemical Reagent.

Preparation of MIL-53(Fe): MIL-53(Fe) was prepared using a modification of the method previously reported.[1] In a typical synthesis, 0.1 mmol of 1, 4-BDC and 0.1 mmol of $FeCl_3 \cdot 6H_2O$ were dissolved in 12 mL of DMF with vigorous stirring to form a homogenous yellow solution. After being stirred for 30 min, the mixture solution was transferred into a Teflon-line stainless steel autoclave of 20 mL capacity, which was heated at a temperature of 160 °C for 12 h and then cooled to room temperature naturally. Finally, the obtained light yellow crystals were collected by centrifugation, washed with distilled water and ethanol, and dried at 60 ℃ under vacuum for further characterization.

Preparation of Fe_3S_4(x wt%)/MIL-53 (x = 0, 31.3, 43.2, 52.1, and 82.8): The hybrid catalysts were prepared by a simple solvothermal method. In detailed, 10 mg of the as-obtained MIL-53(Fe) crystals in light yellow color was dispersed in 10 mL of the anhydrous ethanol under sonication for 15 min to obtain a homogeneous solution; 2.0 mmol of TAA was then added to the solution while stirring for 30 min.

Afterward, the mixture was transferred into a 25 mL of Teflon-lined stainless steel autoclave and maintained at 140℃, 160℃, 180℃ for 3 h, 180℃ for 5 h, respectivity. Then the reaction system was allowed to cool down to room temperature naturally. The resulting products were collected by centrifugation, washed with distilled water and ethanol several times, and then dried at 60℃ under vacuum. Samples with 31.3 wt%, 43.2 wt%, 52.1 wt%, and 82.8 wt% Fe_3S_4 loading were obtained, as measured by inductively coupled plasma-atomic emission spectrometry.

Preparation of Fe_3S_4: Fe_3S_4 was synthesized by a method reported previously.[2] In detail, 0.48 g of $FeCl_3.6H_2O$ (1.78 mmol) and 1.052 g of TAA (14 mmol) were respectively dissolved in 25 mL EG, and the two solutions were mixed together. After being stirred for 30 min, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 2 h. Then the reaction system was allowed to cool down to room temperature naturally. The obtainded product was collected by centrifugation, washed with distilled water and ethanol, and dried at 60 °C under vacuum.

Characterization: X-ray diffraction (XRD) was performed on a Rigaku Ultima IV diffractmeter with Cu Kα radiation (λ=1.5406 Å). The transmission electron microscopy (TEM) image was carried out on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. High-angle annular dark-field scanning transmission spectroscopy (HAADF-STEM) image and corresponding energy-dispersive spectroscopy (EDS) mapping analyses were performed on a JEOL JEM-ARF 200F TEM/STEM with a spherical aberration corrector. The field emission scanning electron microscopy (FESEM) images were taken on a JEOL JSM-6700F SEM. X-ray photoelectron spectra (XPS) was acquired on an ESCALAB MKⅡwith Mg K^{α} as the excitation source. FT-IR spectra (KBr pellets) were conducted on a Thermo Electron NEXUS 670 FTIR spectrometer. The inductively coupled plasma (ICP) emission spectra were carried out on a Perkin Elmer Optima 7300DV ICP emission spectroscope.

Electrochemical measurements: All the electrochemical measurements were performed in a standard three-electrode system using an electrochemical workstation (CHI660E). A saturated calomel electrode (SCE) as the reference electrode, and a graphite rod as the counter electrode, the glassy carbon (GC) disk electrode with catalysts (3 mm in diameter) as the working electrode. Typically, to prepare the working electrode, 4 mg of catalyst with 30 μL Nafion solution (5 wt%) were dispersed in 1 mL of water/ethanol mixture solution (volume ratio of 3:1) with the assistance of sonication for 40 min to form a homogeneous ink. Then, 5 μL of the catalyst ink (containing 20 μg of catalyst) was loaded onto the glassy carbon electrode (catalyst loading 0.285 mg cm^{-2}). Linear sweep voltammetry (LSV) and Cyclic voltammetry (CV) with a scan rate of 5 mV s^{-1} were performed in 0.5 M H_2SO_4. All potentials in this study were calibrated to the reversible hydrogen electrode (RHE) based on the formula $E_{\mathrm{RHE}} = E_{\mathrm{SCE}} + 0.241\mathrm{V} + 0.0591\ \mathrm{pH}\ \mathrm{V}$. The electrochemical impedance spectroscopy was performed in the frequency range from 0.1 to 100 KHz.

S2. Additional characterization information

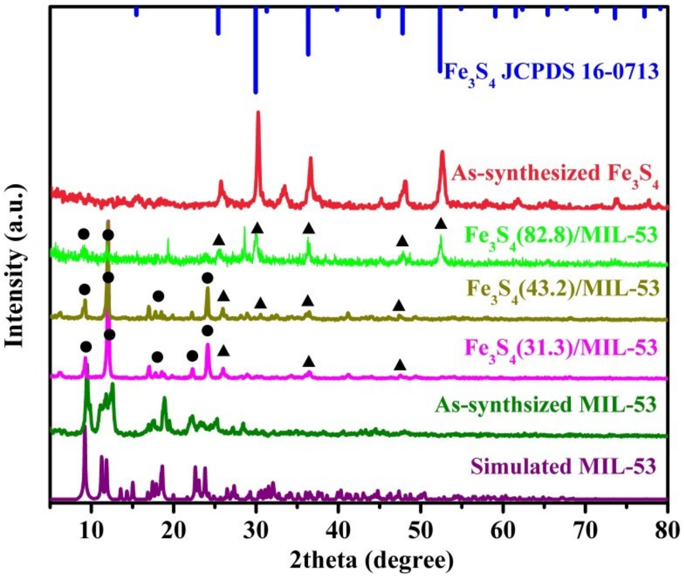

Figure S1. The XRD patterns of simulated MIL-53(Fe), as-obtained MIL-53(Fe), Fe_3S_4 and the other three Fe_3S_4(*x* wt%)/MIL-53(*x* = 31.3, 43.2, 82.8) hybrid catalysts.

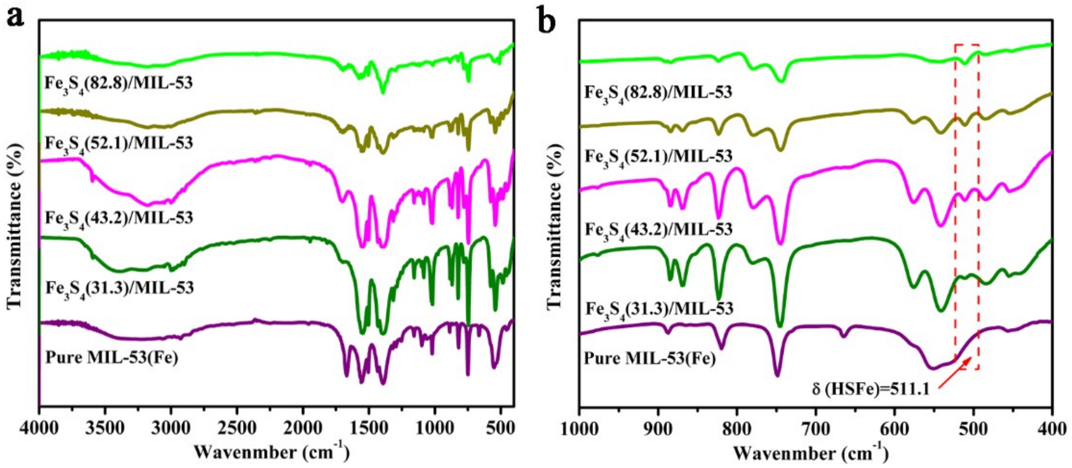

Figure S2. FT-IR spectra of MIL-53(Fe) and Fe_3S_4(*x* wt%)/MIL-53(*x* = 31.3, 43.2, 52.1, 82.8).

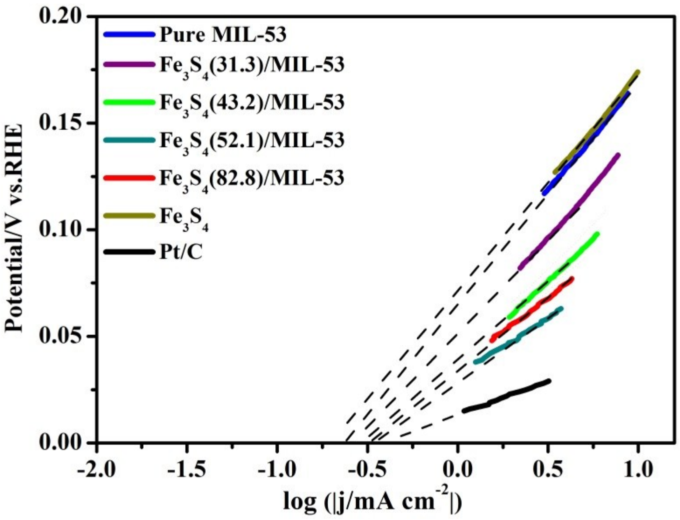

Figure S3. Calculated exchange current densities of various samples by applying extrapolation method to the Tafel plots.

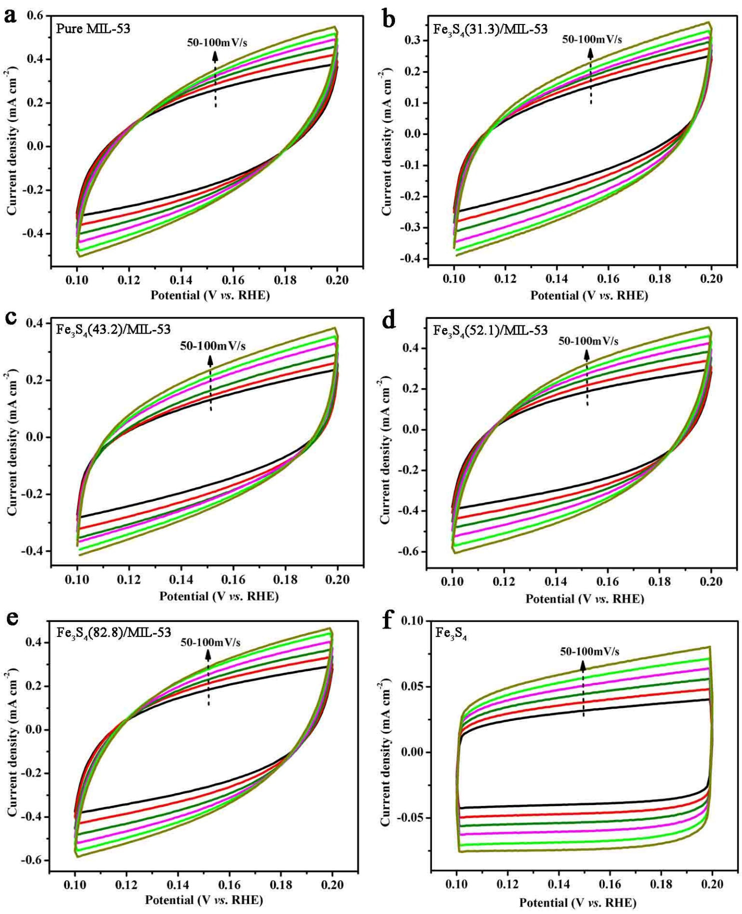

Figure S4. Cyclic voltammetry curves of (a) MIL-53(Fe); (b-e) Fe_3S_4(*x wt%*)/MIL-53(*x* = 31.3, 43.2, 52.1, 82.8) and (f) Fe_3S_4 in the region of 0.1-0.2 V vs. RHE at scan rates from 50 to 100 mV/ s.

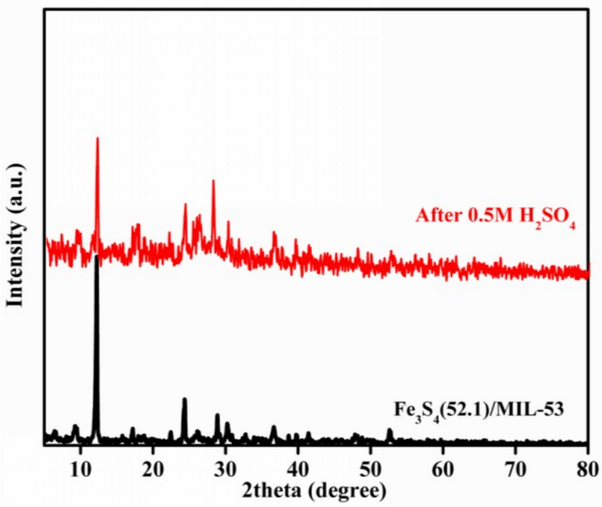

Figure S5. The XRD pattern of Fe_3S_4(52.1 *wt%*)/MIL-53 after the acidic treatment in 0.5 M H_2SO_4 for 50 h.

Table S1. Comparison of HER Parameters of the samples

Catalysts	Onset potential (mV)	**η_{10} (mV)**	**Tafel slope ($mV\cdot dec^{-1}$)**	**Exchange current density j_0 ($\mu A\ cm^{-2}$)**	**Double-layer capacitance C_{dl}($mF\ cm^{-2}$)**
20%Pt/C	0	43	31		
MIL-53(Fe)	104	172	99	229	1.7
Fe_3S_4(31.3)/MIL-53	80	151	93	257	1.75
Fe_3S_4(43.2)/MIL-53	65	121	80	295	1.89
Fe_3S_4(52.1)/MIL-53	48	92	60	363	2.7
Fe_3S_4(82.8)/MIL-53	56	108	69	331	2.3
Fe_3S_4	110	185	101	199	0.7

Table S2| Comparison of HER performance for Fe_3S_4(52.1 wt%)/MIL-53 with other electrocatalysts.

Catalysts	Onset potential(mV)	Tafelslope ($mV \cdot dec^{-1}$)	η_{10} (mV)	Ref.
20%Pt/C	0	31	43	
micro-FeS_2-RGO	70	66	139	(3)
mesoporous FeS_2	30	78	96	(4)
FeS_2	-	62.5	-	(5)
Fe-MoS_2 NF	100	82	136	(6)
($Fe_{0.48}Co_{0.52}$)S_2	143	47.5	196	(7)
$Fe_{1-x}Co_xS_2$/CNT	-	46	120/20	(8)
Fe_3S_4(52.1 wt%)/MIL-53	48	60	92	*This work*

Reference:

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