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Fe-doped CoS_2 Nano-octahedra as Electrocatalysts for Hydrogen Evolution Reaction in Acidic Medium

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1. Electrochemical Analysis:

1.1 Electrochemical Active Surface Area (ECSA) Calculation:

To evaluate the electrochemical active surface area (ECSA), cyclic voltammograms (CVs) were recorded within the non-Faradaic potential region at different scan rates. The electrochemical double-layer capacitance (C_{dl}) was determined from the slope of the linear fit obtained by plotting the capacitive current $(i_{anodic} - i_{cathodic})/2$ versus scan rate. The ECSA was then calculated using:

$$\text{ECSA} = \frac{C_{dl}}{C_s}$$

Where C_s = 0.04 mF cm^{-2} is the specific capacitance of a smooth planar surface, and C_{dl} represents the electrochemical double-layer capacitance extracted from the slope of the capacitive current versus scan rate plot.

1.2 Mass Activity Calculation:

The mass activity of an electrocatalyst is a measure of the catalyst's efficiency per unit mass, which can be calculated using the following formula:

$$\textbf{Mass Activity (A/g)} = \frac{Current\ Density\ (A/cm^2)}{Mass\ of\ Electrocatalyst\ (g)}$$

Where, Current Density (A/cm^2) is the current per unit electrode area at a specific potential (200 mV). Mass of Electrocatalyst (g) refers to the amount of the catalyst used, typically in grams.

1.3 Specific Activity Calculation:

The Specific activity of an electrocatalyst is a measure of the intrinsic catalytic activity of the surface, which can be calculated using the following formula:

$$\textbf{Specific Activity (mA/ } cm^2\textbf{)} = \frac{Current\ Density\ (A/cm^2)}{ECSA\ (cm^2)}$$

Where, Current Density (A/cm²) is the current per unit electrode area at a specific potential (200 mV). Electrochemically active surface area (cm²) refers to the surface area of the catalyst used, typically in cm².

1.4 Turn Over Frequency Calculation:

Turnover Frequency (TOF) is a measure of the intrinsic catalytic activity of a material. It represents the number of hydrogen molecules generated per active site per second.

$$\text{TOF} = \frac{I}{2 \times F \times n}$$

Where I is the current (A) at a specific potential, (F) is Faraday's constant (96485 C/mol), and (n) is the number of moles of metal active sites. The value of n was calculated based on the catalyst mass loading and the atomic weight of the metal, assuming all metal atoms are electrochemically active.

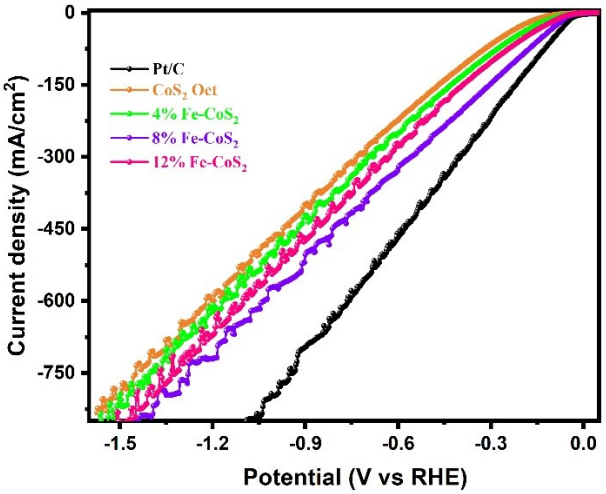

Figure S1. Extended polarization (LSV) curves of Pt/C, CoS_2-Oct, 4% Fe-CoS_2, 8% Fe-CoS_2 & 12% Fe-CoS_2 catalysts recorded in acidic medium

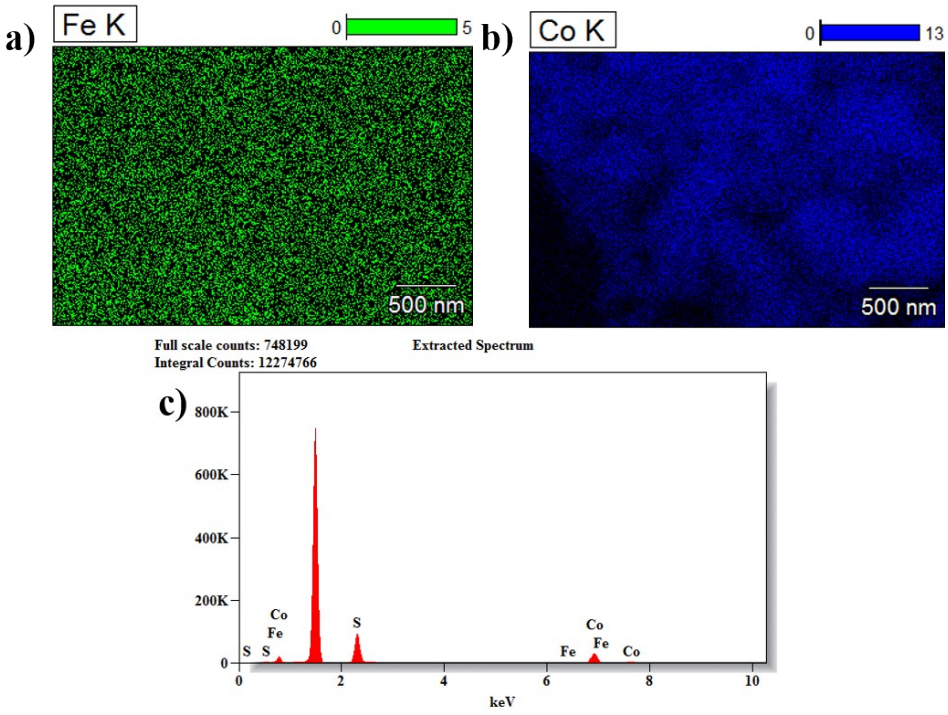

Figure S2. Elemental mapping images of the 4% Fe-CoS_2 octahedra showing the distribution of (a) Fe and (b) Co, (c) EDS spectra

Element	Extracted Spectrum	Extracted Spectrum	Extracted Spectrum	Extracted Spectrum	Extracted Spectrum
	Net Counts	Weight %	Atom %	Atom % err	Chemical Formula
S K	1383749	52.66	67.13	0.23	S
Fe K	14863	1.09	0.80	0.05	Fe
Co K	570315	46.25	32.07	0.10	Co
		100.00	100.00		

Table S1. Elemental composition of 4% Fe-CoS_2 determined from EDS analysis.

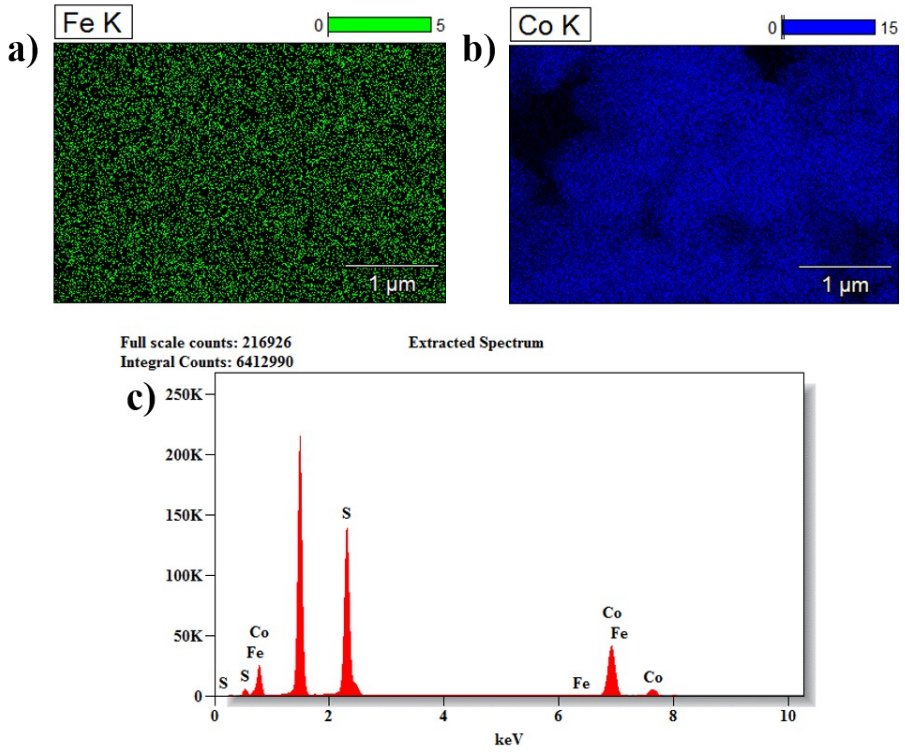

Figure S3. Elemental mapping images of the 8% Fe-CoS_2 octahedra showing the distribution of (a) Fe and (b) Co, (c) EDS spectra

Element	Extracted Spectrum	Extracted Spectrum	Extracted Spectrum	Extracted Spectrum	Extracted Spectrum
	Net Counts	Weight %	Atom %	Atom % err	Chemical Formula
S K	1860971	53.57	67.95	0.23	S
Fe K	3705	0.21	0.15	0.01	Fe
Co K	748452	46.22	31.90	0.08	Co
		100.00	100.00		

Table S2. Elemental composition of 8% Fe-CoS_2 determined from EDS analysis.

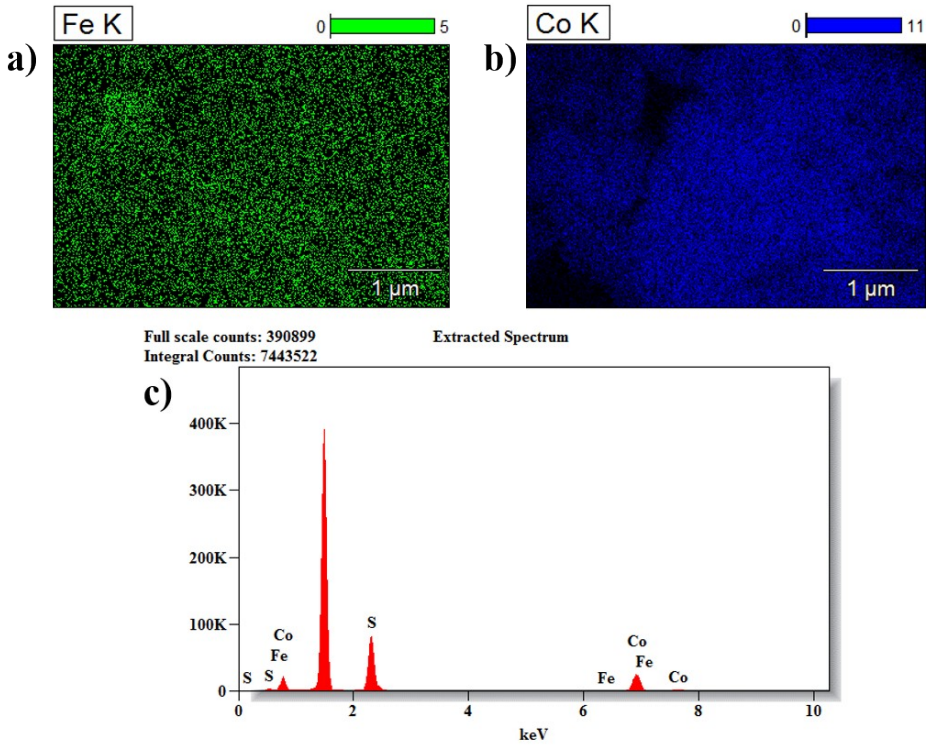

Figure S4. Elemental mapping images of the 12% Fe-CoS_2 octahedra showing the distribution of (a) Fe and (b) Co, (c) EDS spectra

Element	Extracted Spectrum	Extracted Spectrum	Extracted Spectrum	Extracted Spectrum	Extracted Spectrum
	Net Counts	Weight %	Atom %	Atom % err	Chemical Formula
S K	1229844	53.68	68.02	0.24	S
Fe K	16272	1.38	1.01	0.04	Fe
Co K	478592	44.94	30.97	0.10	Co
		100.00	100.00		

Table S3. Elemental composition of 12% Fe-CoS_2 determined from EDS analysis.

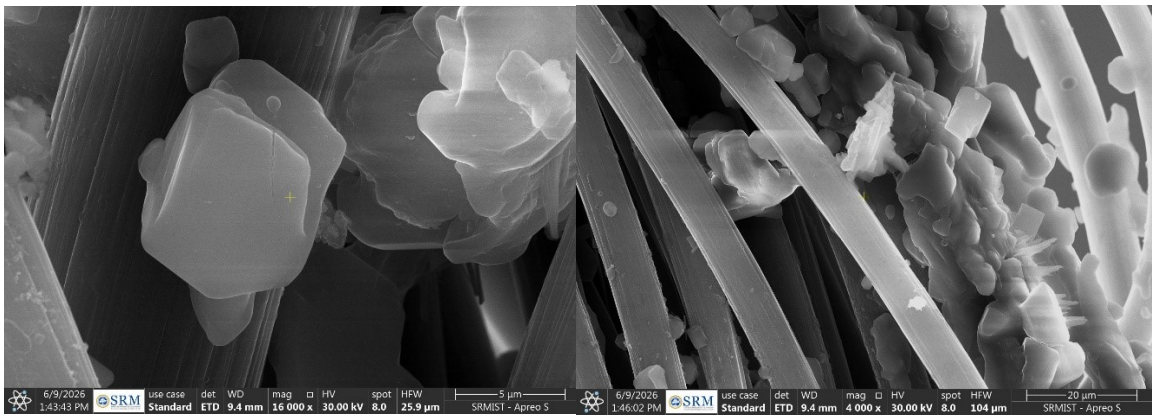

Figure S5. SEM images of the 8% Fe-CoS_2 catalyst after 96 h chronopotentiometric HER stability testing in 0.5 M H_2SO_4.

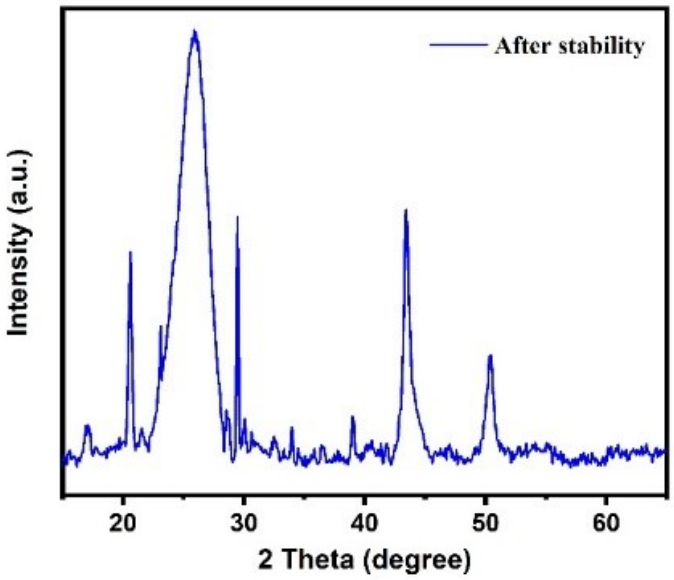

Figure S6. XRD pattern of the 8% Fe-CoS_2 catalyst after 96 h HER stability testing in 0.5 M H_2SO_4.

Electrocatalyst	η_{HER} (mV)	Tafel (mV/dec)	Reference
Fe/P-CoS_2	80	56	[1]
Co:FeS_2/CoS_2NWs	69	46	[2]
CoS_2/CNT	155	59	[3]
CoS_2-CFN	136	73	[4]
CoS_2-Oct	173	76	[4]
3% CoS_2-7% CuS	62	46	[5]
MoS_2/CoS_2/CC)	87	73	[6]
CoS_2/CoSe@C	164	42	[7]
WS_2/CoS_2/CC	146	64	[8]
CoS_2-MoS_2 Nanoflower	153	71	[9]
8% Fe-CoS_2	**57**	**56**	**This work**

Table S4. Comparison of the electrocatalytic activity of Fe-CoS_2 catalysts with recently reported papers for HER in 0.5 M H_2SO_4

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