Supplementary Information

Exploring the electrocatalytic activity of cobalt disulfide nanosheets towards hydrogen evolution reaction with *in situ* ECAFM

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3.1.1 SEM and XRD

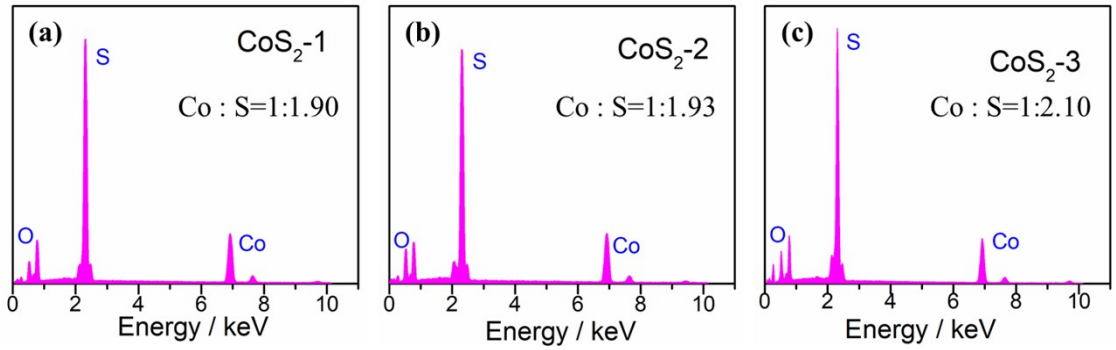

Figure S1. EDX of (a) CoS_2-1, (b) CoS_2-2, (c) CoS_2-3.

3.2.1 Basic electrocatalytic property

Hydrogen evolution reaction (HER) is a multi-step electrochemical process which generates gaseous hydrogen from the surface of an electrode. According to the classic theory, the rection mechanism in acid and alkaline media could be described by the following Eqs.S1-S5 [1-3].

(1) Volmer reaction

$$H^+ + M + e^- \leftrightharpoons M-H_{ads} \text{ (acid media)} \quad (1)$$

$$H_2O + M + e^- \leftrightharpoons M-H_{ads} + OH^- \text{ (alkaline media)} \quad (2)$$

(2) Heyrovsky reaction

$$M-H_{ads} + H^+ + e^- \leftrightharpoons M + H_2 \text{ (acid media)} \quad (3)$$

$$M-H_{ads} + H_2O + e^- \leftrightharpoons M + OH^- + H_2 \text{ (alkaline media)} \quad (4)$$

(3) Tafel reaction

$2M-H_{ads} \leftrightharpoons 2M + H_2$ (both acid and alkaline media) (5)

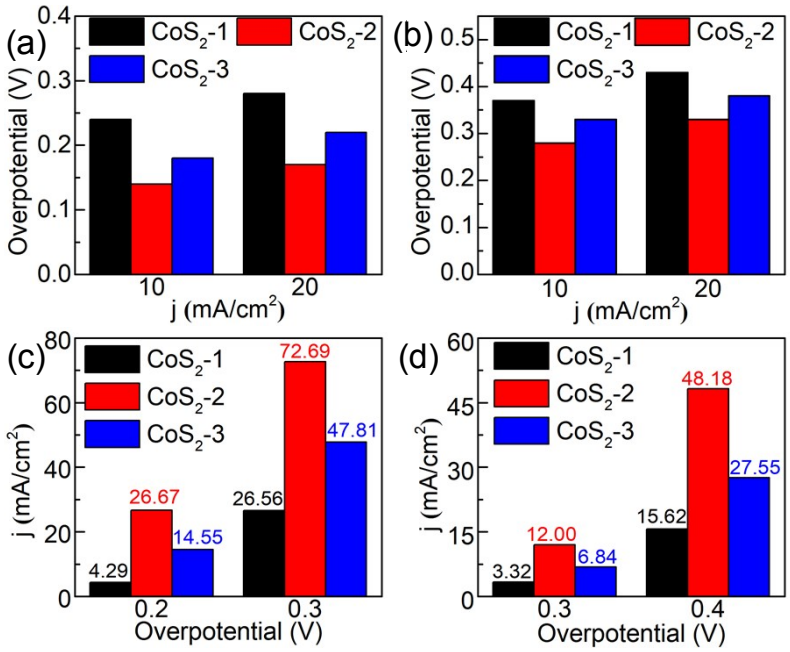

Figure S2. v-j graphs in 0.5 M H_2SO_4 (a) and 1.0 M KOH (b) solutions, and j-v graphs (c) in 0.5 M H_2SO_4 and 1.0 M KOH (d) solutions.

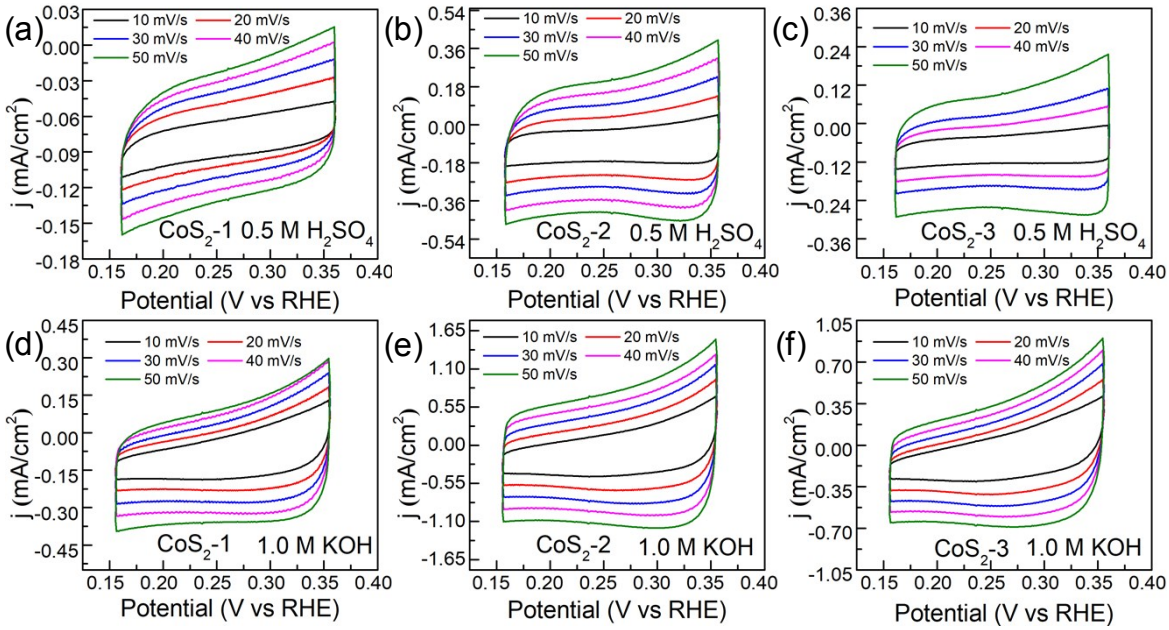

Figure S3. CV curves at different scan rates (10-50 $mV \cdot s^{-1}$) of the as-prepared (a) CoS_2-1, (b) CoS_2-2, (c) CoS_2-3 in acidic solutions and (d) CoS_2-1, (e) CoS_2-2, (f) CoS_2-3 in alkaline solutions.

The electrochemical active surface area (ECSA) is calculated through Eq. S6 [4, 5].

$$\mathbf{ESCA=C_{dl}/C_s} \quad \mathbf{(6)}$$

Where C_s is the specific capacitance of the sample or the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions. Based on typical reported values, C_s = 0.040 mF cm^{-2} in 1M KOH solutions and C_s = 0.035 mF cm^{-2} in 0.5 M H_2SO_4 solutions [6]. In this work, the ECSA was estimated to be 28.57, 297.14 and 97.14 cm^2 in 0.5 M H_2SO_4 solutions for CoS_2-1, CoS_2-2 and CoS_2-3 catalysts, while in 1M KOH solutions was 90, 400 and 207.5 cm^2, respectively. These ECSA values were used for the specific activity calculated in the following section.

The Specific Activity (SA) is calculated through Eq. S7 [5].

$$\textbf{SA (mA cm}^{-2}\textbf{)}=J/\textbf{ECSA} \qquad (7)$$

Where J is the current density (mA cm^{-2}).

The Mass Activity (MA) is calculated through Eq. S8 [5].

$$\textbf{MA (mA mg}^{-1}\textbf{)} = J/\textbf{m} \qquad (8)$$

Where J is the current density (mA cm^{-2}), m is mass loading (mg cm^{-2}).

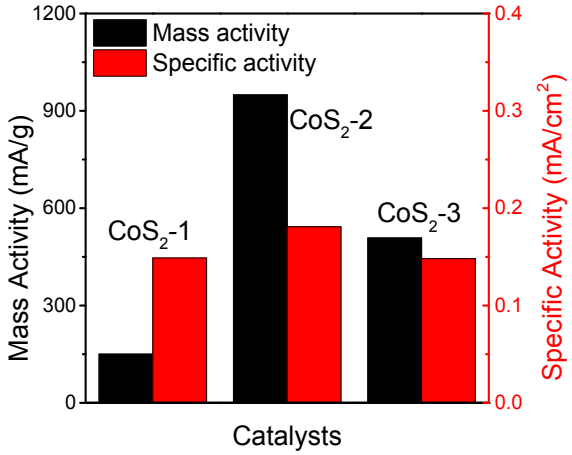

Figure S4. Mass activity and specific activity of the catalysts at an overpotential of 200 mV for HER in acidic solutions.

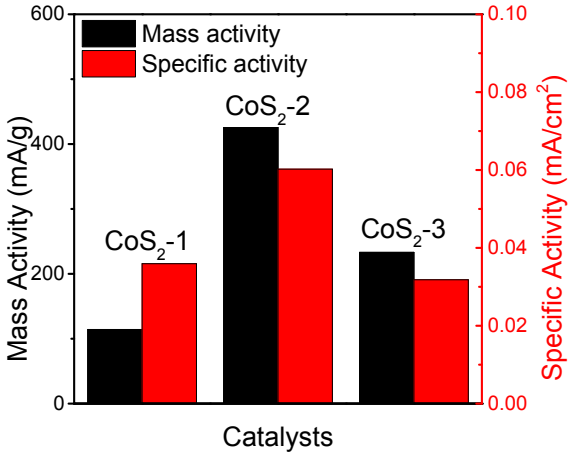

Figure S5. Mass activity and specific activity of the catalysts at an overpotential of 300 mV for HER in alkaline solutions.

Table S1 HER performances for some reported base metals electrocatalysts.

Catalysts	Overpotential η(mV) at corresponding j	Current density j (mA/cm^2)	Tafel slope (mV/dec)	Electrolytes	References
CoS_2 nanosheet	145	10	26	0.5 M H_2SO_4	This work
	289	10	105	1.0 M KOH	This work
CoS_2 nanowire/CC	161	10	90	1.0 M KOH	[7]
CoS_2 microwire	158	10	58	0.5 M H_2SO_4	[8]
$CoNi_2S_4$	255	10	85	1.0 M KOH	[9]
Ni/Co/MoS_2 nanoboxes	155	10	51	0.5 M H_2SO_4	[10]
CoS_2	273	10	133	1.0 M KOH	[11]
CoS_x/MoS_2	239	10	103	0.5 M H_2SO_4	[12]
CoS_2/MoS_2	173	10	61	0.5 M H_2SO_4	[13]
Co_3S_4/MoS_2	210	10	88	0.5 M H_2SO_4	[14]

3.2.3 FESEM and XPS of CoS_2-2 after HER catalysis

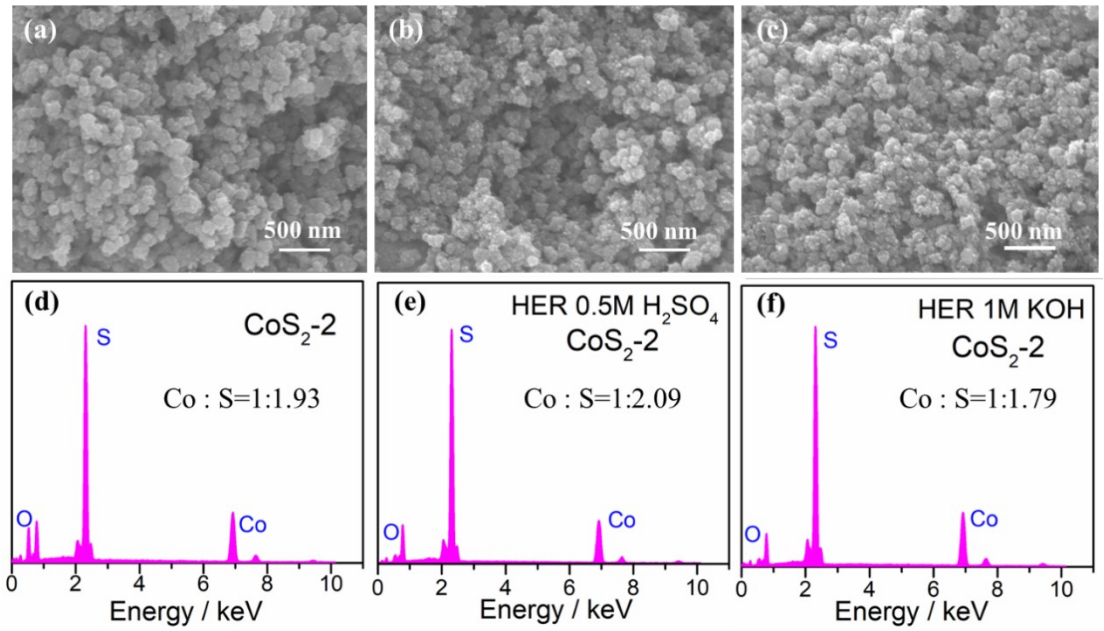

Figure S6. FESEM morphologies of (a) the as-prepared CoS_2-2 samples, (b) after HER in 0.5 M H_2SO_4 solutions, (c) after HER in 1.0 M KOH solutions, and (d-f) their corresponding EDX.

Reference

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