Supporting Information

Trivalent Europium Ions Doped WO_3/WS_2 Semiconductor Heterostructure Interface for Efficient Hydrogen Evolution Reactions under Acidic and Alkaline Dual Conditions

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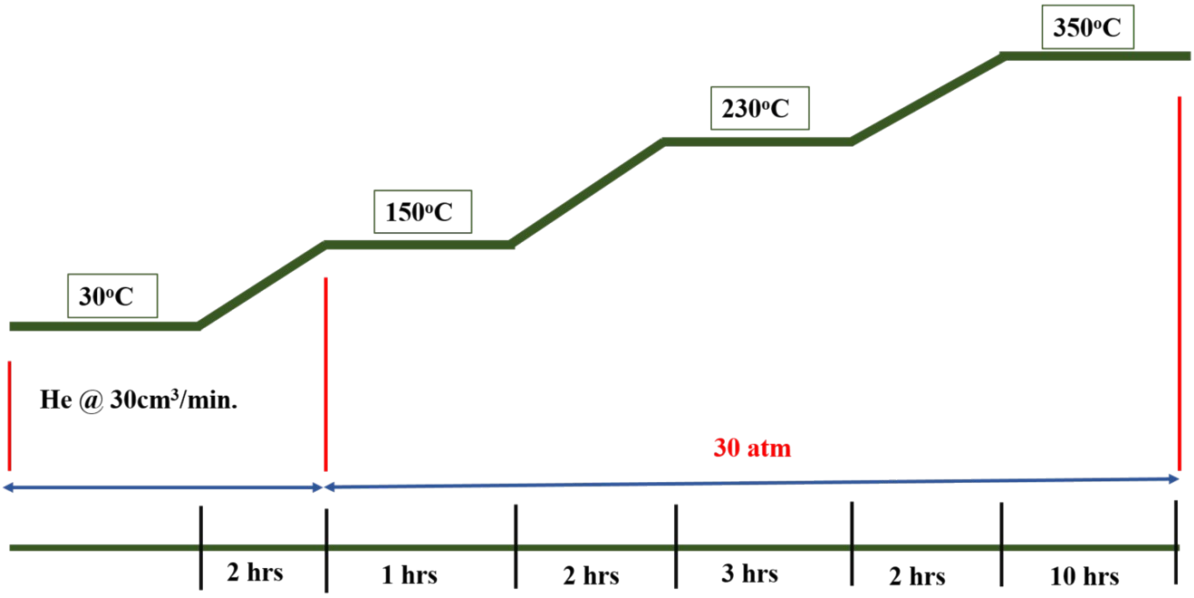


Figure S1: Sulfidation process steps in the reactor to prepare Eu^{3+}:WO_3/WS_2 heterostructure.

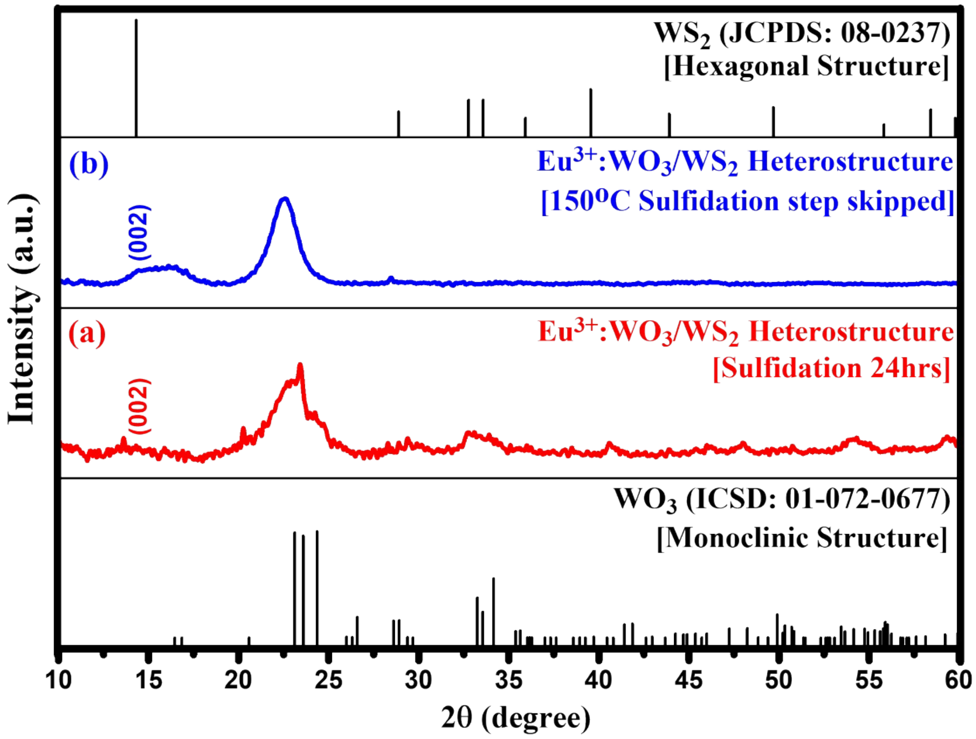


Figure S2: XRD pattern of prepared (a) $Eu^{3+}:WO_3/WS_2$ semiconductor heterostructure (Sulfidation for 24hrs) and (b) $Eu^{3+}:WO_3/WS_2$ semiconductor heterostructure (150°C Sulfidation step skipped) SCNMs.

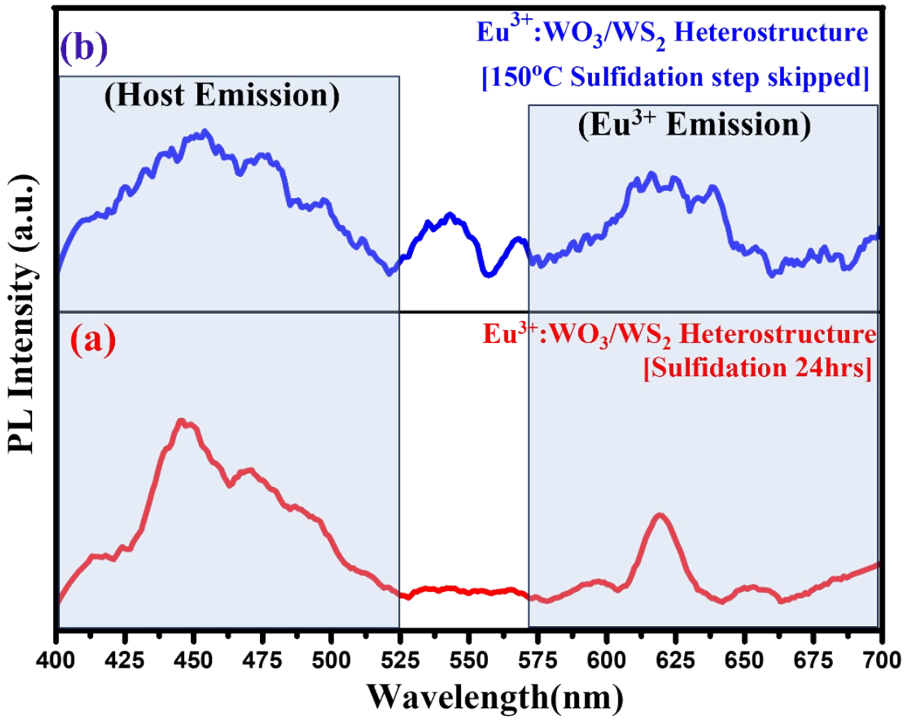


Figure S3: PL emission spectra of prepared (a) $Eu^{3+}:WO_3/WS_2$ semiconductor heterostructure (Sulfidation for 24hrs) and (b) $Eu^{3+}:WO_3/WS_2$ semiconductor heterostructure (150°C Sulfidation step skipped) SCNMs.

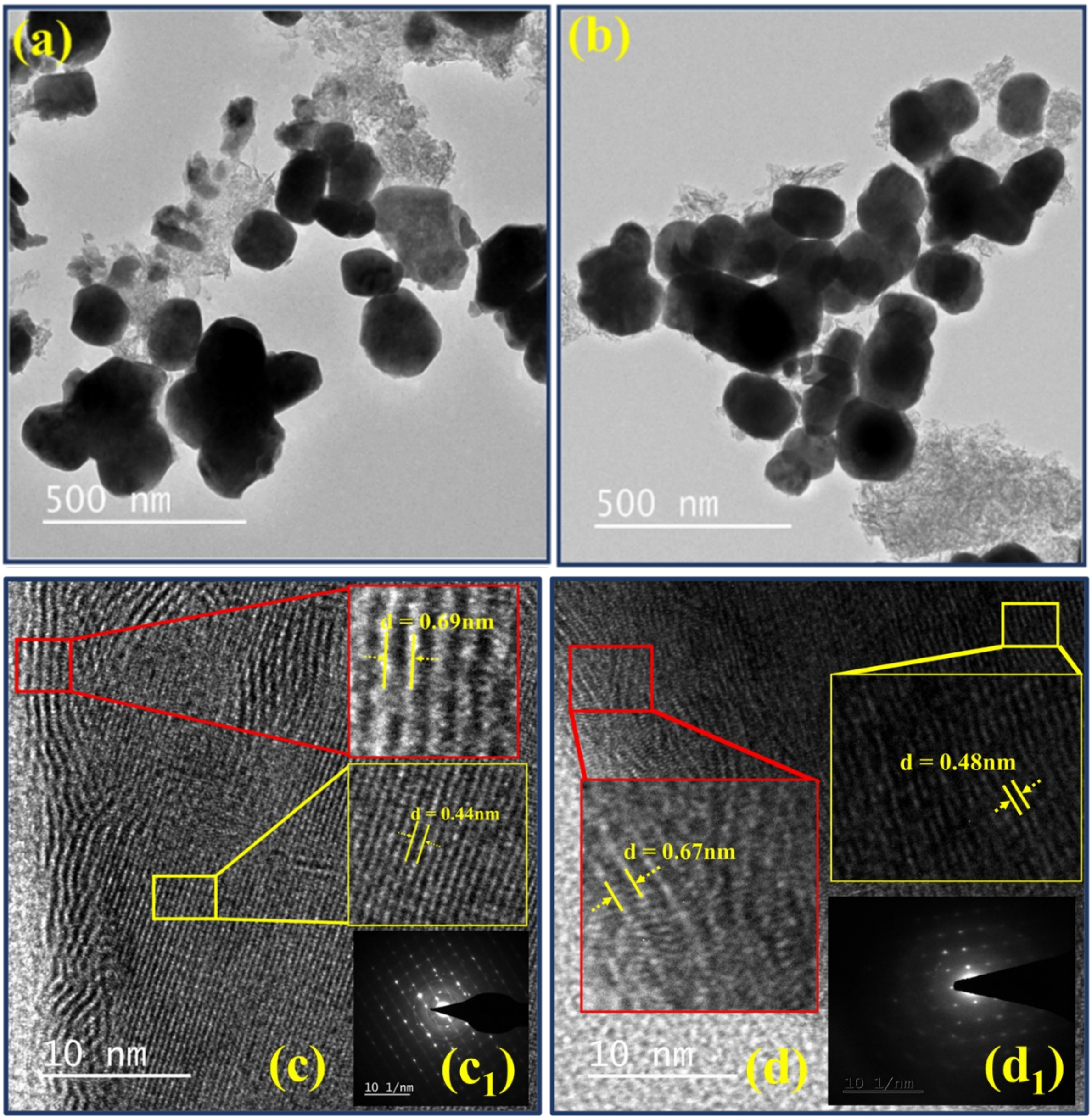


Figure S4: TEM image of (a) Eu^{3+}:WO_3/WS_2 semiconductor heterostructure (Sulfidation for 24hrs) & (b) Eu^{3+}:WO_3/WS_2 semiconductor heterostructure (150°C Sulfidation step skipped); (c) and inset c_1: SAED pattern of Eu^{3+}:WO_3/WS_2 semiconductor heterostructure (Sulfidation 24hrs) and (d) and inset d_1: SAED pattern of Eu^{3+}:WO_3/WS_2 semiconductor heterostructure (150°C Sulfidation step skipped).

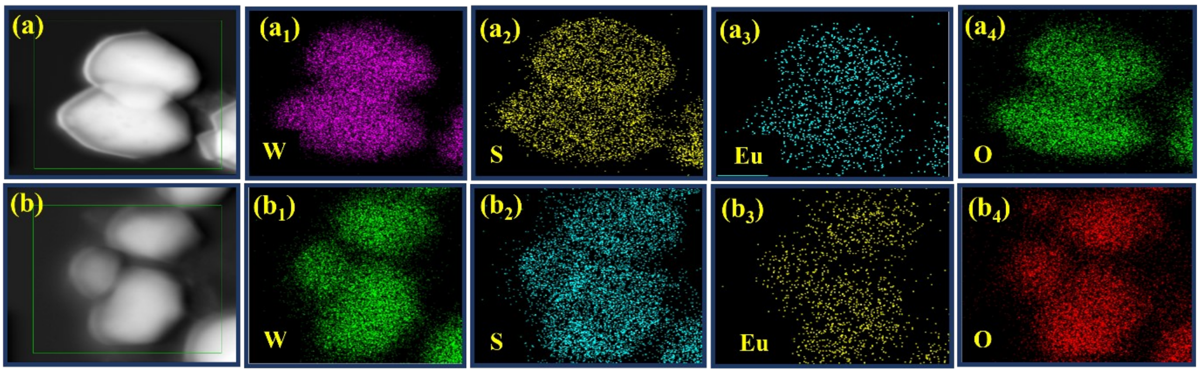
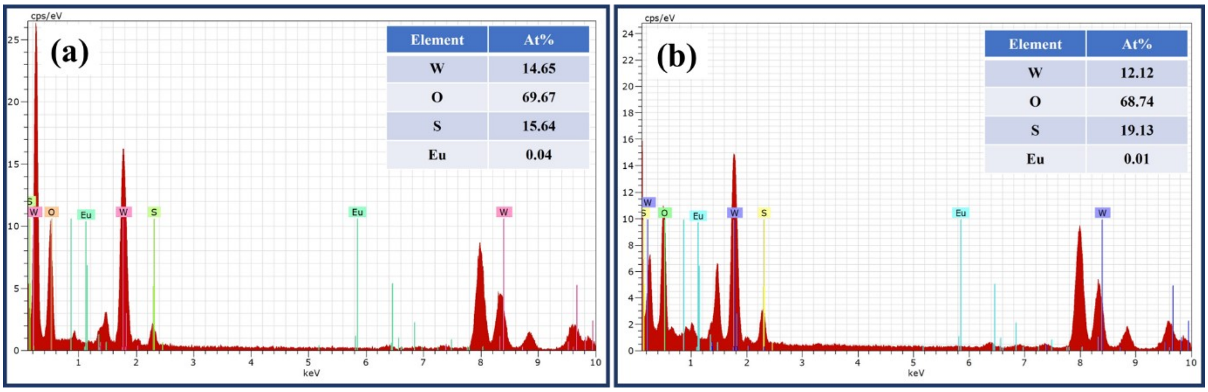


Figure S5: Elemental mapping of (a; a_1-a_4) Eu^{3+} :WO_3/WS_2 semiconductor heterostructure (Sulfidation for 24hrs) and (b; b_1-b_4) Eu^{3+}:WO_3/WS_2 semiconductor heterostructure (150°C Sulfidation step skipped).



(a)

Element	At%
W	14.65
O	69.67
S	15.64
Eu	0.04

(b)

Element	At%
W	12.12
O	68.74
S	19.13
Eu	0.01

Figure S6: EDAX spectrum of (a) Eu^{3+}:WO_3/WS_2 semiconductor heterostructure (Sulfidation for 24hrs) and (b) Eu^{3+}:WO_3/WS_2 semiconductor heterostructure (150°C Sulfidation step skipped).

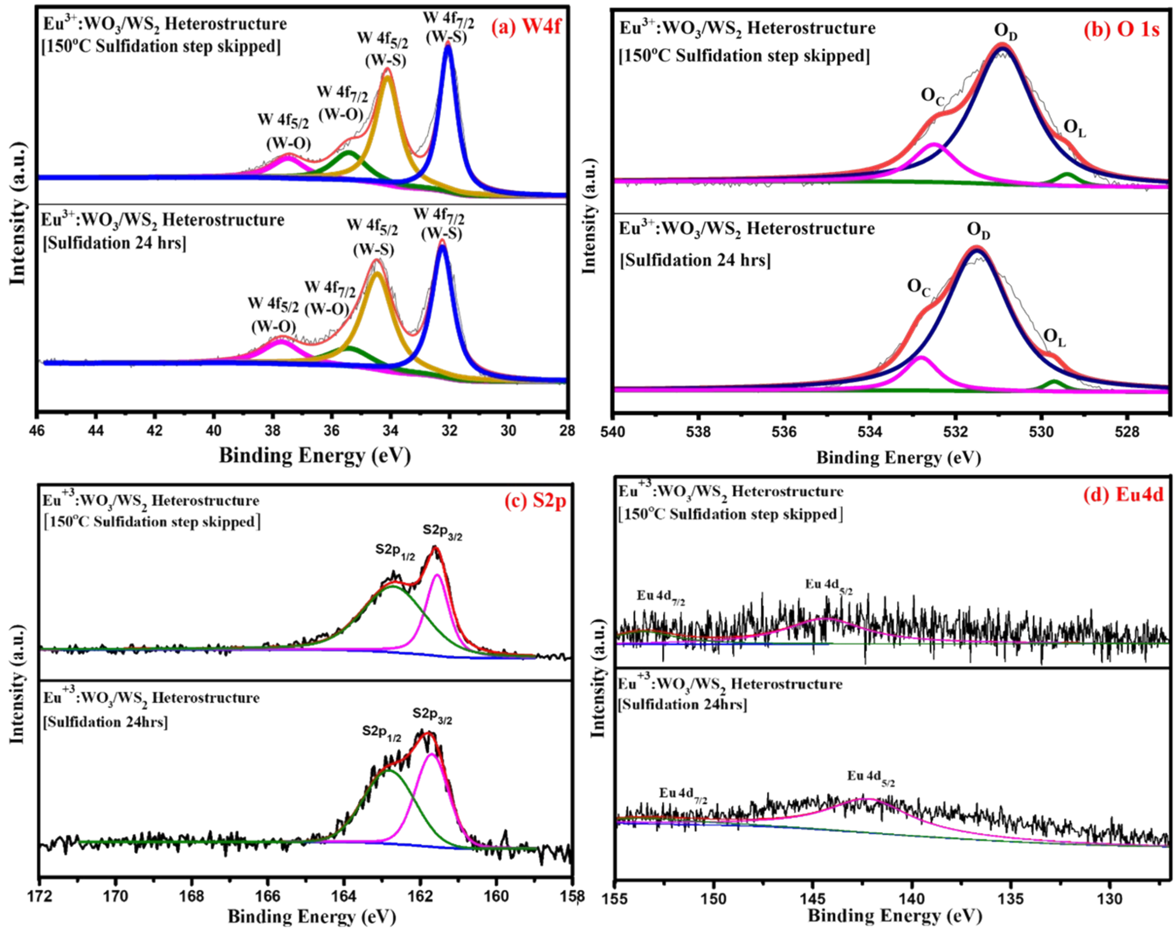


Figure S7: XPS deconvoluted spectra of (a) W4f, (b) O1s, (c) S2p and (d) Eu4d for Eu^{3+}:WO_3/WS_2 semiconductor heterostructure (Sulfidation for 24hrs) and (b) Eu^{3+}:WO_3/WS_2 semiconductor heterostructure (150°C Sulfidation step skipped), respectively.

Degree of Sulfurization Determination

The degree of sulfurization was determined using the given formula;

$$Area\% = \frac{Peak\ area\ of\ W^{4+}}{Peak\ area\ of\ W^{4+}\ + Peak\ area\ of\ W^{6+}} \times 100$$

The calculated sulfide conversion percentages were found to be 18.6%, 14%, and 15.8% for the Eu^{3+}:WO_3/WS_2 heterostructures subjected to 10-hour sulfidation, 24-hour sulfidation, and the sample with the 150°C sulfidation step skipped, respectively. These results indicate that the 10-hour sulfidation process achieved the highest degree of sulfur incorporation, further validating its effectiveness in optimizing the WO_3 to WS_2 transformation for enhanced hydrogen evolution reaction performance.

BET

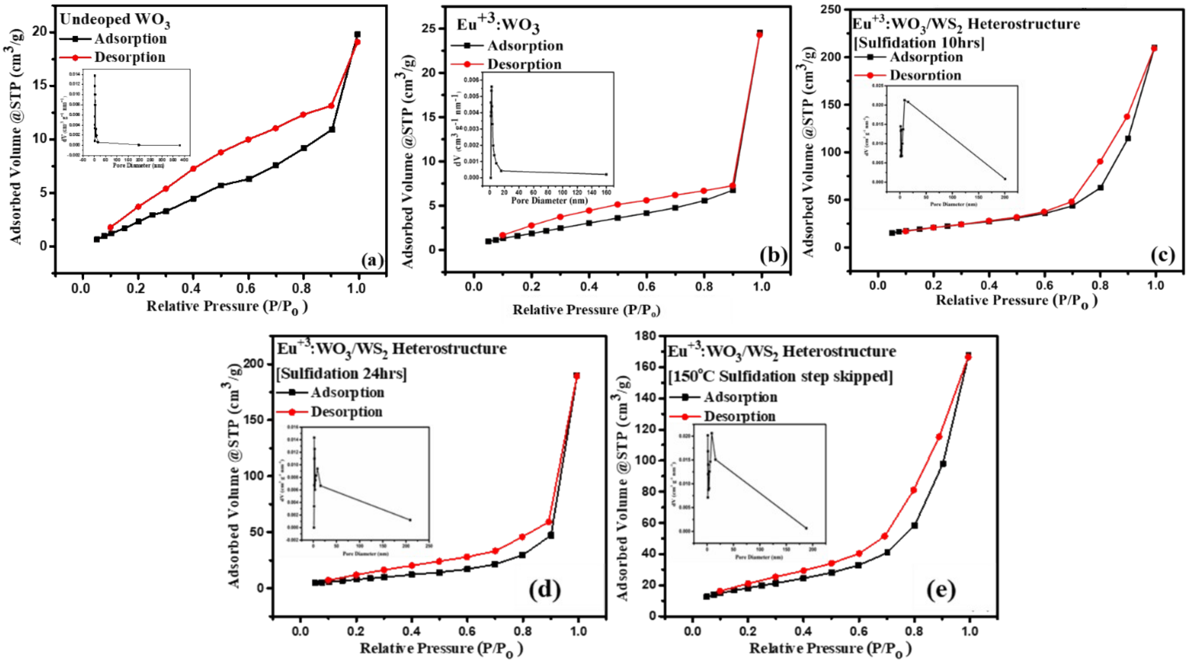


Figure S8: BET of (a) undoped WO_3 (b) $Eu^{3+}:WO_3$, and (c) $Eu^{3+}:WO_3/WS_2$ semiconductor heterostructure (Sulfidation for 10hrs), (d) $Eu^{3+}:WO_3/WS_2$ semiconductor heterostructure (Sulfidation for 24hrs), and (e) $Eu^{3+}:WO_3/WS_2$ semiconductor heterostructure (150°C Sulfidation step skipped).

Sample Name	BET Surface area (m^2/g)
Undoped WO_3	8.19
$Eu^{+3}:WO_3$	9.68
$Eu^{+3}:WO_3/WS_2$ Heterostructure (Sulfidation 10hrs)	75.47
$Eu^{+3}:WO_3/WS_2$ Heterostructure (Sulfidation 24hrs)	31.81
$Eu^{+3}:WO_3/WS_2$ Heterostructure (150°C Sulfidation step skipped)	68.03

Table S1: Surface area obtained using BET measurement for each synthesized material.

CV Curves

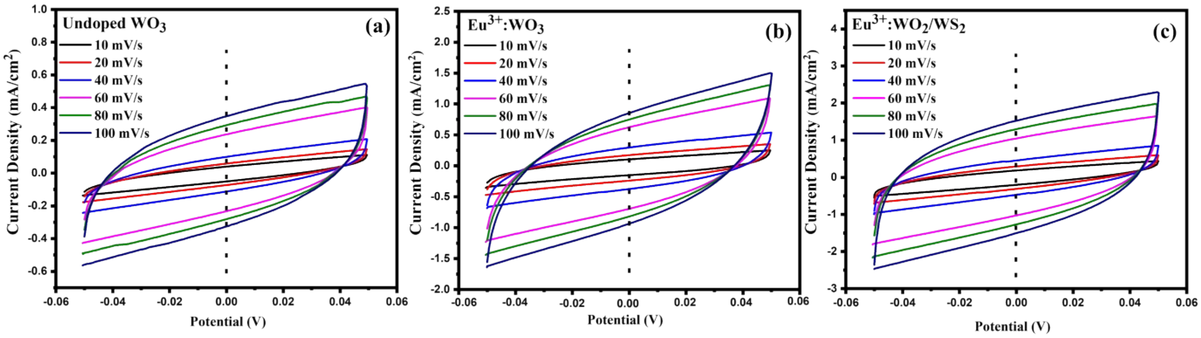


Figure S9: Cyclic voltammograms of (a) undoped WO_3 (b) $Eu^{3+}:WO_3$, and (c) $Eu^{3+}:WO_3/WS_2$ semiconductor heterostructure, which were recorded in acidic electrolyte at different scan rates.

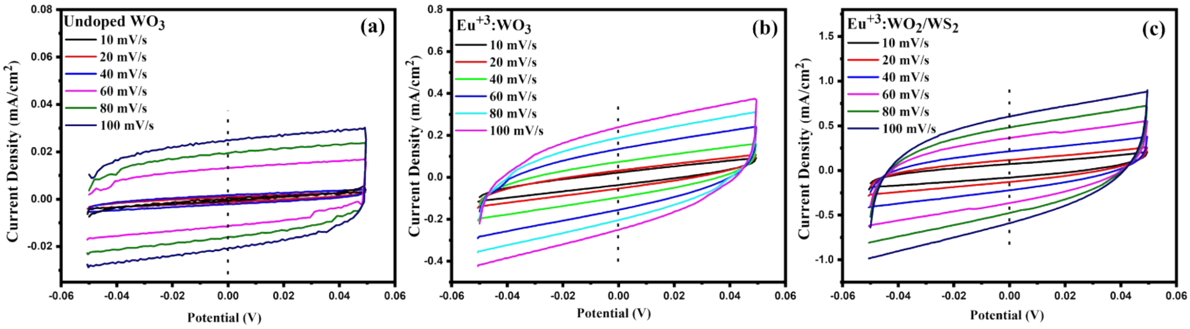


Figure S10: Cyclic voltammograms of (a) undoped WO_3 (b) Eu^{3+}:WO_3, and (c) Eu^{3+}:WO_3/WS_2 semiconductor heterostructure, which were recorded in alkaline electrolyte at different scan rates.

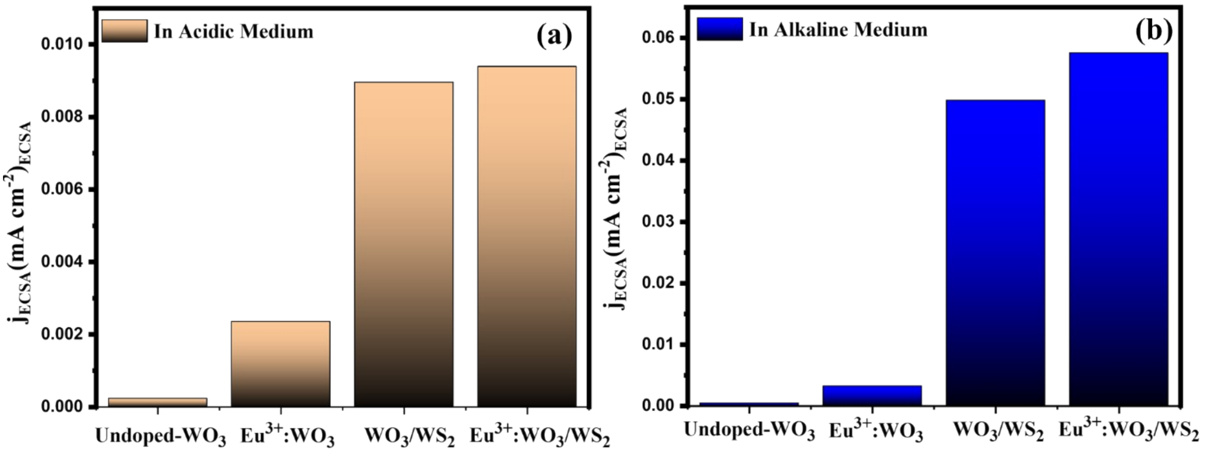


Figure S11: Comparison of electrochemically active surface area (ECSA)-normalized HER current densities for different catalysts in (a) 0.5 M H_2SO_4 and (b) 1M KOH electrolytes.

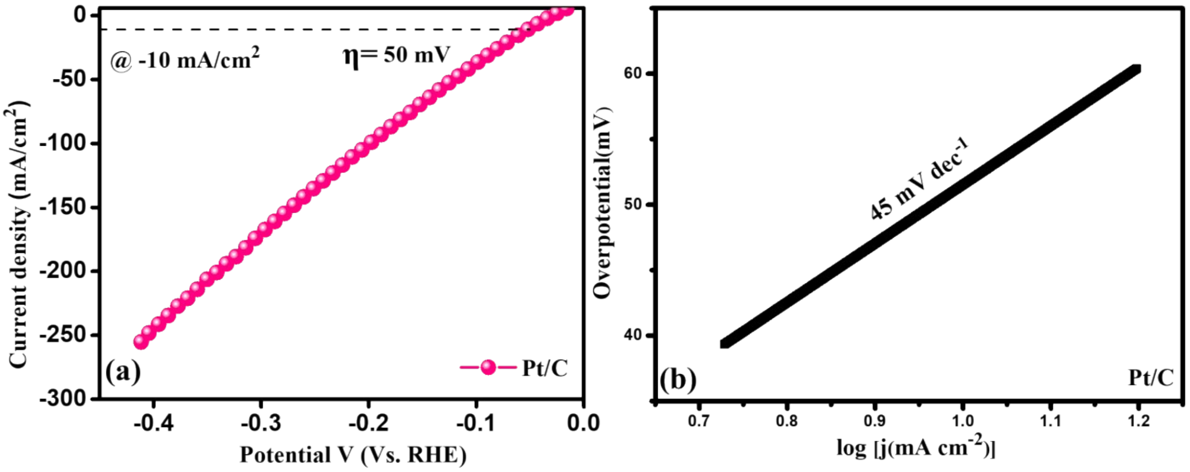


Figure S12: (a) Linear sweep voltammetry curve of Pt/C and (b) Tafel slope for Pt/C in 0.5M H_2SO_4 electrolyte.

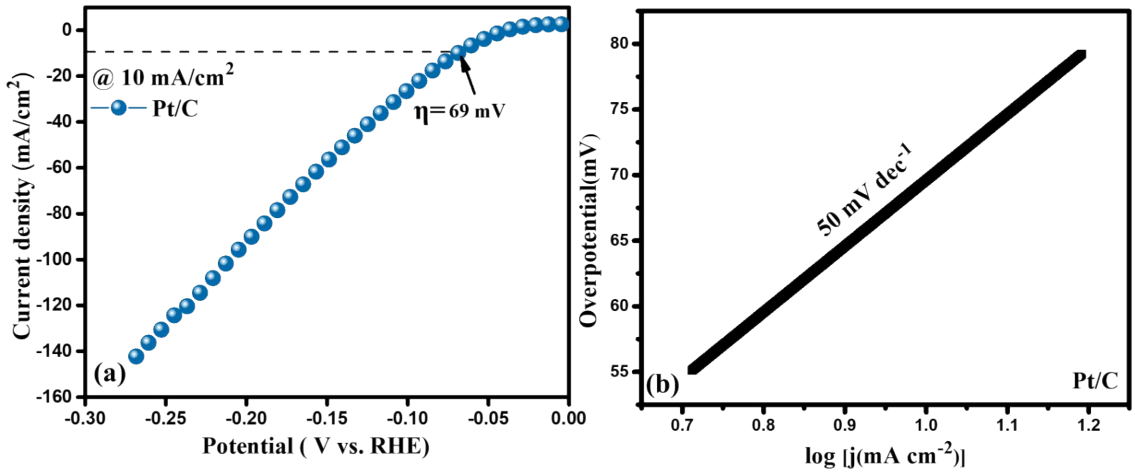


Figure S13: (a) Linear sweep voltammetry curve of Pt/C and (b) Tafel slope for Pt/C in 1M-KOH electrolyte.

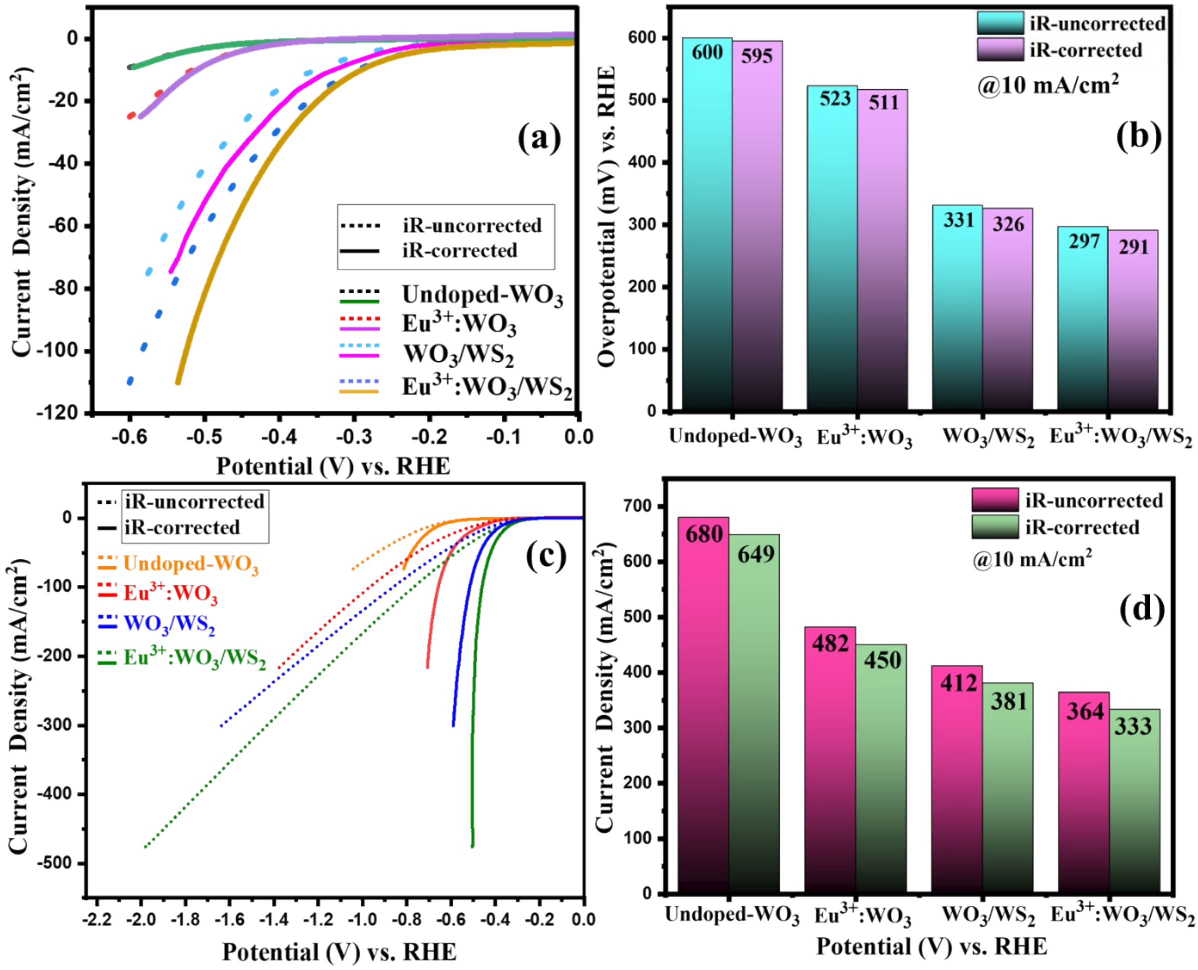
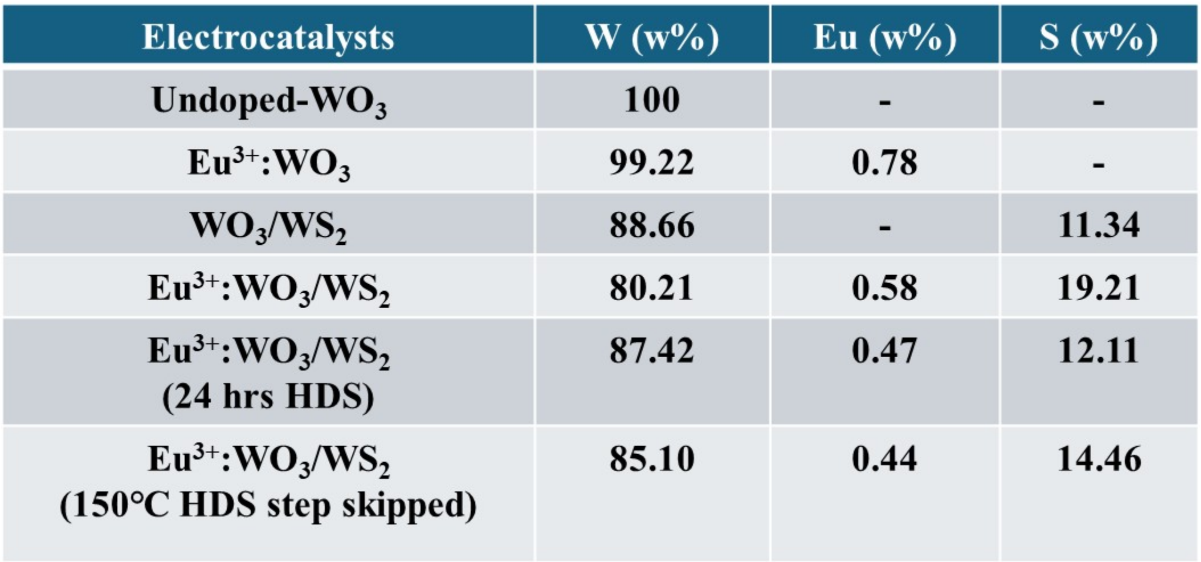


Figure S14: Electrocatalytic HER performance. (a) iR-corrected and uncorrected LSV curves for all catalysts at 5 mV s^{-1} in 0.5M H_2SO_4 electrolyte and (b) the corresponding overpotentials at 10 mA cm^{-2}; (c) iR-corrected and uncorrected LSV curves for all catalysts at 5 mV s^{-1} in 1M KOH electrolyte and (d) the corresponding overpotentials at 10 mA cm^{-2}.

Table S2: Comparative data with previously reported work.

Electrocatalysts	Electrolyte (HER)	Overpotential (mV) @ 10mA/cm^2	Tafel Slope (mV/dec)	Electrodes	Ref.
(5%) Co-doped WO_3-WS_2	0.5M H_2SO_4 0.5M KOH	~321 ~337	-	RE: Ag/AgCl CE: Graphite Rod	[1]
Ag-doped WO_3 nanoplates	0.1M H_2SO_4	~530	40	RE: Hg/Hg_2Cl_2 CE: Pt Electrode	[2]
WS_2 Nanosheets	0.5M H_2SO_4	~337	80	RE: Ag/AgCl CE: Graphite Rod	[3]
WS_2/WO_3 Heterostructure	0.5M H_2SO_4	~395	50	RE: Ag/AgCl CE: Pt Foil	[4]
1T-WS_2/a-WO_3	0.5M H_2SO_4	~212	-	RE: Ag/AgCl CE: Pt Electrode	[5]
Ir-WS_2 (9.8 at%)	1M-KOH 1 M Na_2SO_4	~248 ~548	49 89	-	[6]
Ta-doped WO_3 nanowires	1M H_2SO_4	~520	-	RE: Ag/AgCl CE: Pt Wire	[7]
P-doped WS_2	0.5M H_2SO_4	~245	123	RE: Ag/AgCl CE: Pt Electrode	[8]
Solution-processed WS_2	0.5M H_2SO_4	~410	71	RE: Hg/HgCl CE: Pt wire	[9]
(1%) Eu^{3+}:WO_3/WS_2 Heterostructure	**0.5M H_2SO_4**	**~291**	**149**	**RE: Hg/Hg_2Cl_2** **CE: Graphite Rod**	**This work**
	1M KOH	**~333**	**114**	**RE: Hg/HgO** **CE: Graphite Rod**	

Table S3: Elemental composition obtained from XRF excluding oxygen:



Electrocatalysts	W (w%)	Eu (w%)	S (w%)
Undoped-WO_3	100	-	-
Eu^{3+}:WO_3	99.22	0.78	-
WO_3/WS_2	88.66	-	11.34
Eu^{3+}:WO_3/WS_2	80.21	0.58	19.21
Eu^{3+}:WO_3/WS_2 (24 hrs HDS)	87.42	0.47	12.11
Eu^{3+}:WO_3/WS_2 (150°C HDS step skipped)	85.10	0.44	14.46

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