Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Efficient Hydrogen Evolution from the Hole-Degenerate-Doped WS_2 Electrocatalyst Over a Wide pH Range

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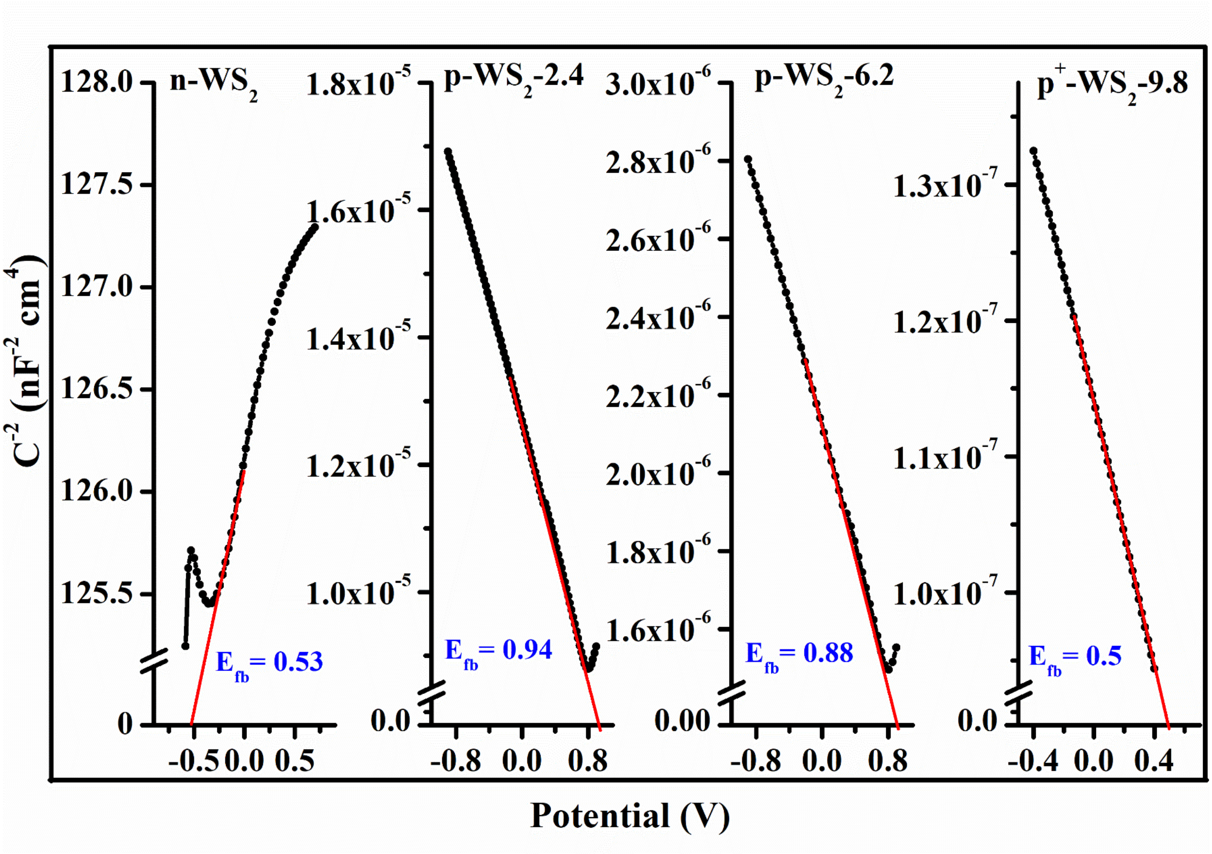


Fig. S1 : Simulated Mott-Schottky plots of *n*-WS_2, *p*-WS_2-2.4, *p*-WS_2-6.2 and *p*⁺-WS_2-9.8 semiconductor electrocatalysts generated from SCAPS software

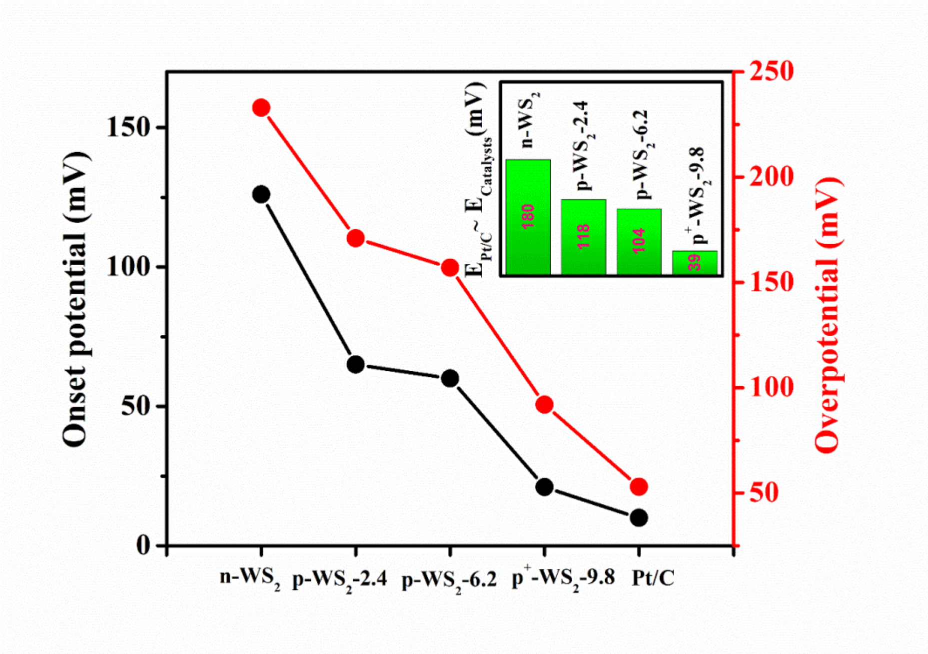


Fig. S2 Variation of onset potential (@ 1 mA cm^{-2}) and overpotentials (@ 10 mA cm^{-2}) of all catalysts for different Ir concentration in 0.5M H_2SO_4 electrolyte. The overpotential difference from the standard Pt/C ($E_{Pt/C}$-$E_{catalyst}$) electrode at j=10 mA cm^{-2} shown in inset.

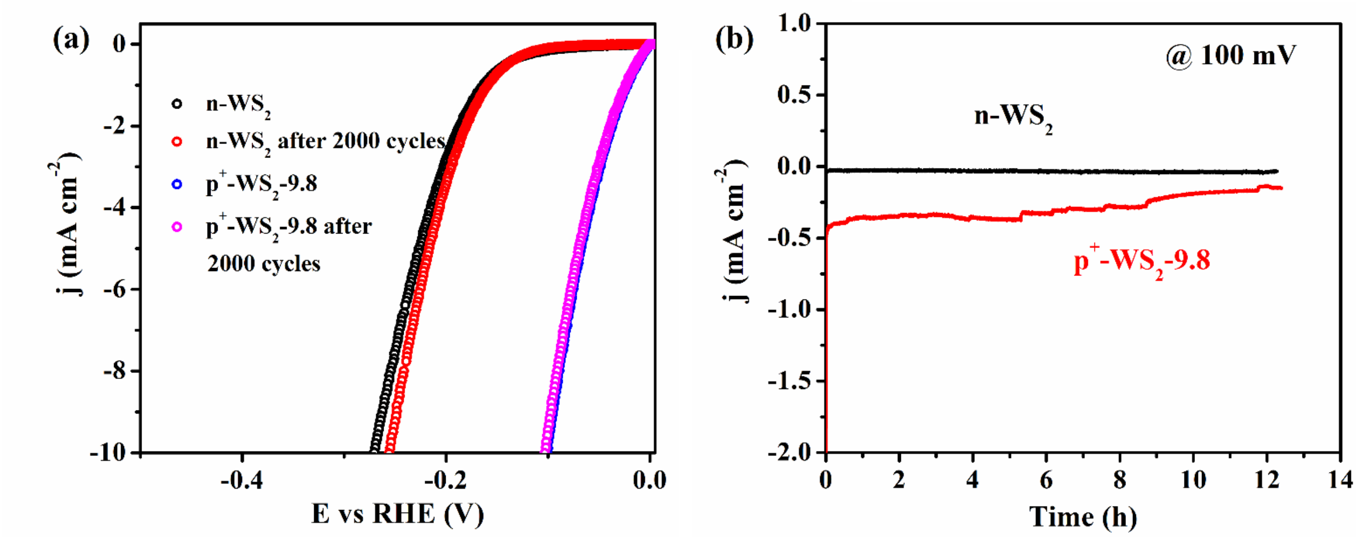


Fig. S3 (a) Comparative cyclic voltrametry stability test data for 2000 cycles and (b) chronoampeometry durability measurment of n-WS$_2$ and p^+-WS$_2$-9.8 electrocatalysts in 0.5M H_2SO_4 electrolyte

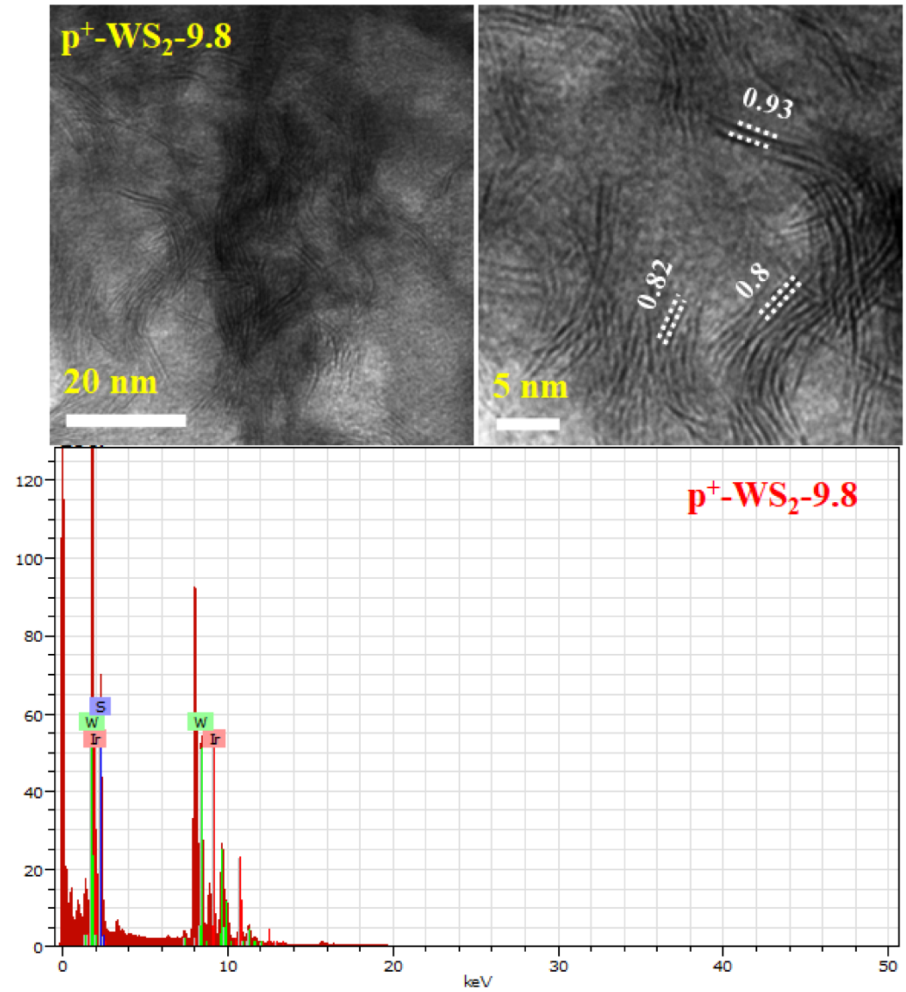
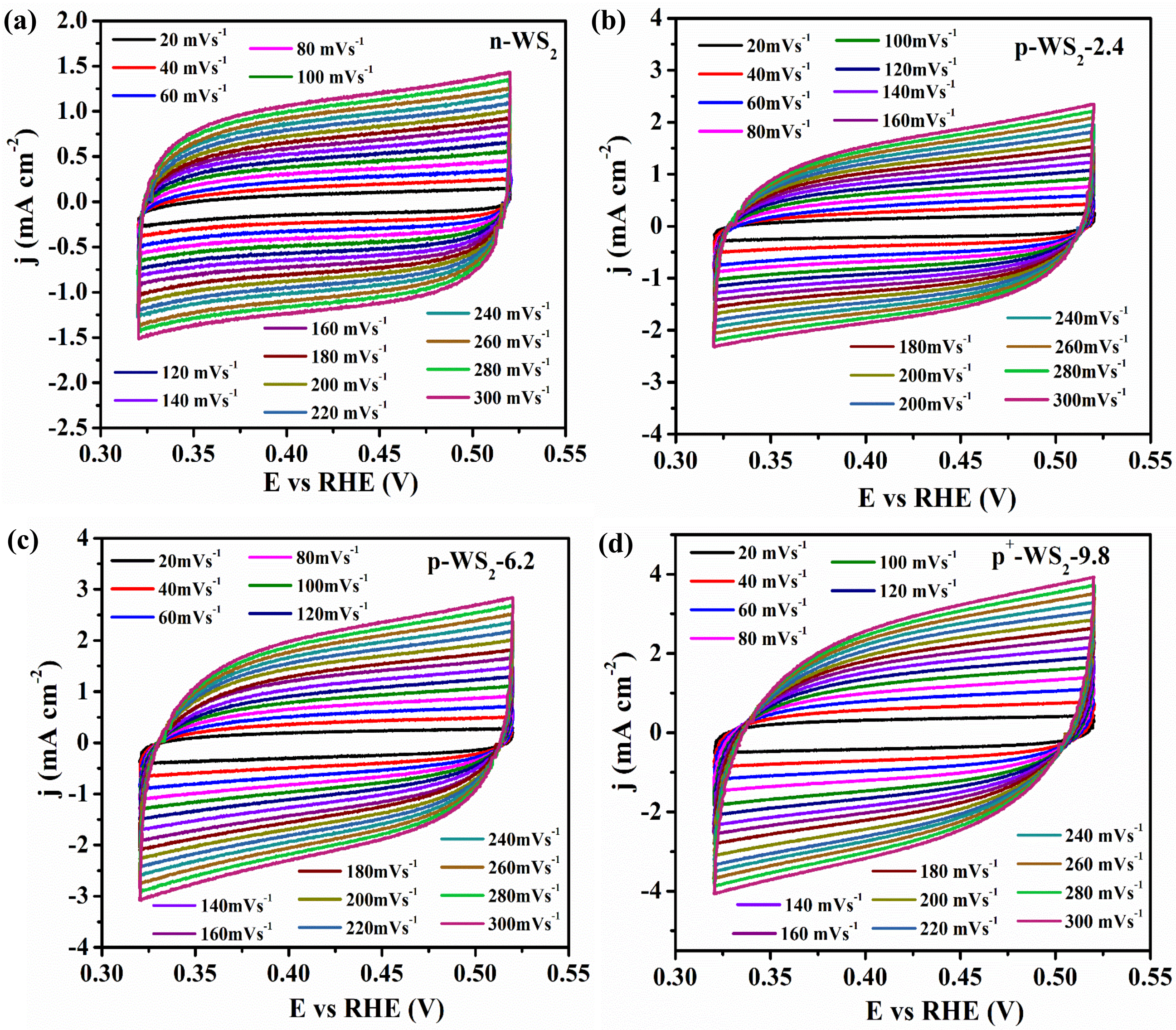


Fig. S4 (a) Low and (b) high-resolution TEM images, and (c) EDX spectra of *p*+-WS_2-9.8 after 2000 cycles voltrametry stability in 0.5M H_2SO_4 electrolyte



(a)
n-WS2
20 mVs-1
40 mVs-1
60 mVs-1
80 mVs-1
100 mVs-1
120 mVs-1
140 mVs-1
160 mVs-1
180 mVs-1
200 mVs-1
220 mVs-1
240 mVs-1
260 mVs-1
280 mVs-1
300 mVs-1
j (mA cm-2)
E vs RHE (V)
(b)
p-WS2-2.4
20mVs-1
40mVs-1
60mVs-1
80mVs-1
100mVs-1
120mVs-1
140mVs-1
160mVs-1
180mVs-1
200mVs-1
200mVs-1
240mVs-1
260mVs-1
280mVs-1
300mVs-1
j (mA cm-2)
E vs RHE (V)
(c)
p-WS2-6.2
20mVs-1
40mVs-1
60mVs-1
80mVs-1
100mVs-1
120mVs-1
140mVs-1
160mVs-1
180mVs-1
200mVs-1
220mVs-1
240mVs-1
260mVs-1
280mVs-1
300mVs-1
j (mA cm-2)
E vs RHE (V)
(d)
p+-WS2-9.8
20 mVs-1
40 mVs-1
60 mVs-1
80 mVs-1
100 mVs-1
120 mVs-1
140 mVs-1
160 mVs-1
180 mVs-1
200 mVs-1
220 mVs-1
240 mVs-1
260 mVs-1
280 mVs-1
300 mVs-1
j (mA cm-2)
E vs RHE (V)

Fig. S5 Cyclic voltametry curve of of *n*-WS_2, *p*-WS_2-2.4, *p*-WS_2-6.2 and p^+-WS_2-9.8 semiconductors catalysts for different scan rate measured in 0.5 M H_2SO_4 electrolyte. .

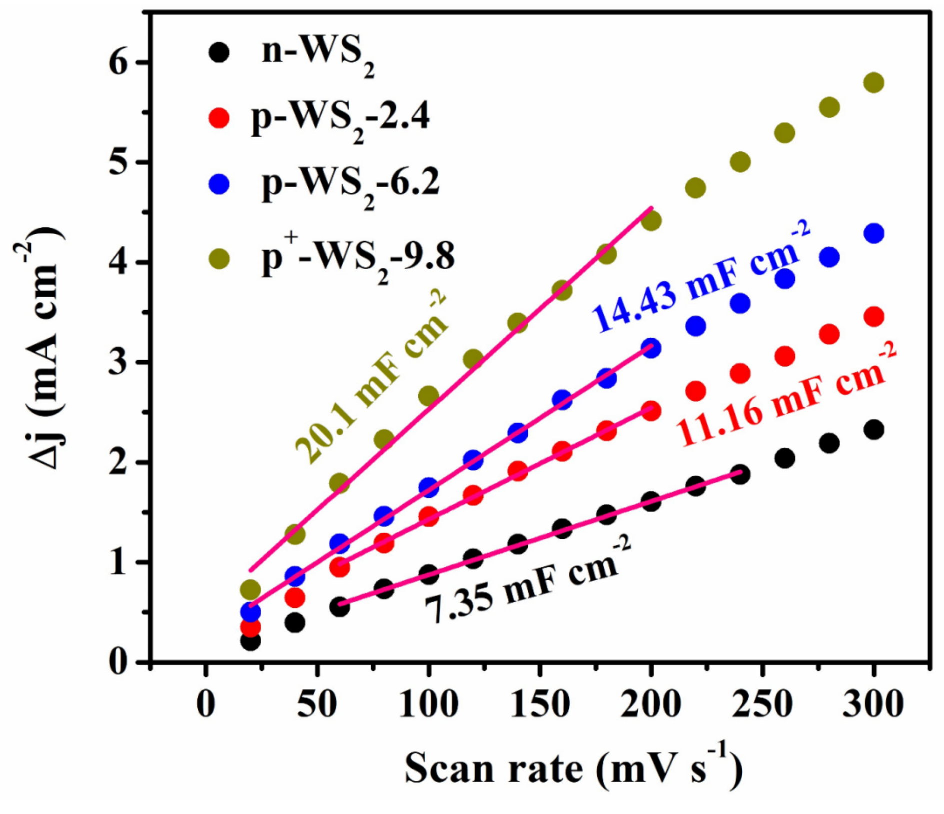


Fig. S6 Specific capacitance data of *n*-WS_2, *p*-WS_2-2.4, *p*-WS_2-6.2, and p^+-WS_2-9.8 electrocatalysts measured in 0.5M H_2SO_4 electrolyte.

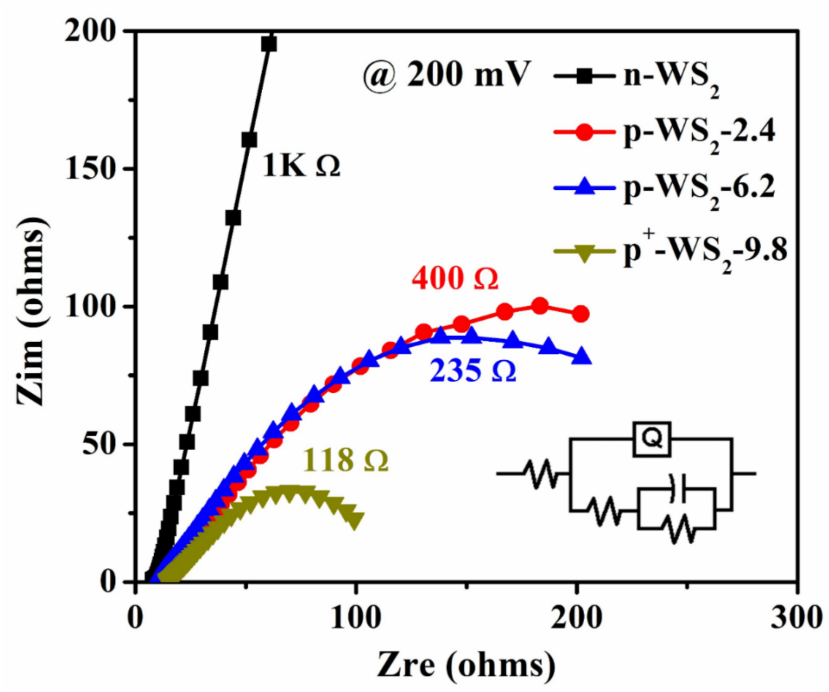
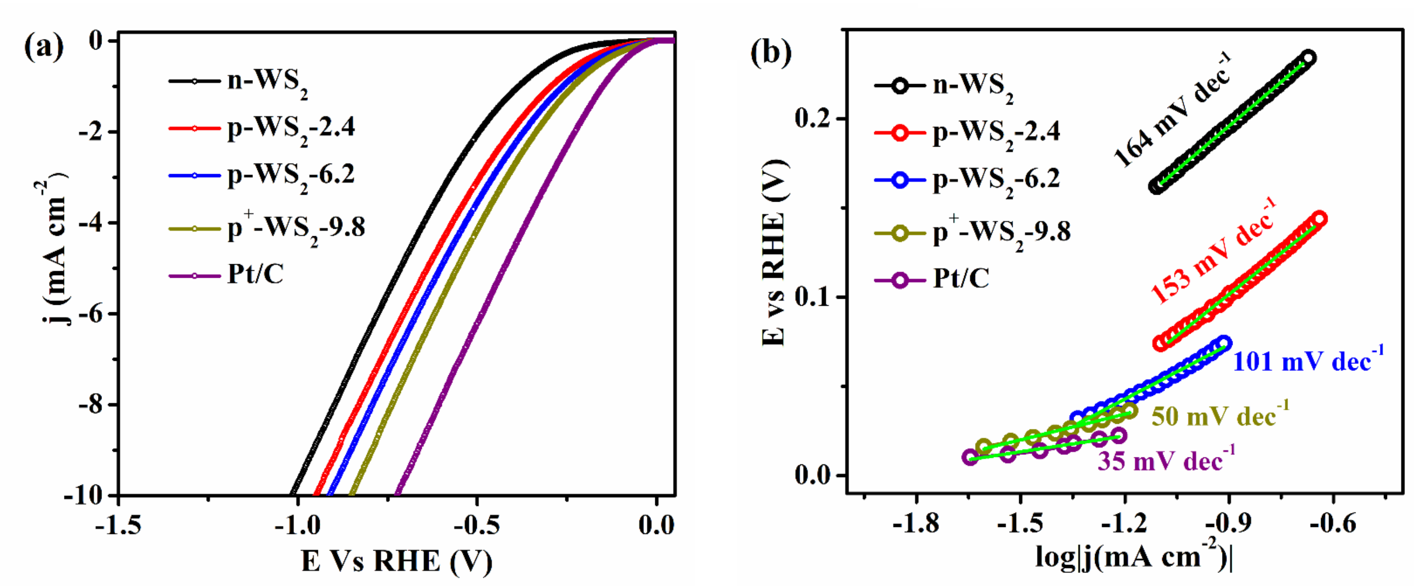


Fig. S7 Nyquist plots of *n*-WS_2, *p*-WS_2-2.4, *p*-WS_2-6.2, and *p*$^+$-WS_2-9.8 electrocatalysts measured in 0.5M H_2SO_4 electrolyte



affinity (eV)				
Effective DOS CB (cm^{-3})	2.02×10^{19}	2.02×10^{19}	2.02×10^{19}	2.02×10^{19}

Fig. S8 (a) HER polarization with corresponding (d) Tafel plots of *n*-WS_2, *p*-WS_2-2.4, *p*-WS_2-6.2, and *p*$^{+}$-WS_2-9.8 measured in 0.01 M KOH electrolyte (pH = 12).

Effective DOS VB (cm^{-3})		$2.48x10^{19}$	$2.48x10^{19}$	$2.48x10^{19}$	$2.48x10^{19}$	
Electron mobility (cm^2/Vs)		200	200	200	200	
Hole mobility (cm^2/Vs)		50	50	50	50	
Doping density (cm^{-3})		$8x10^{17}$	$3x10^{18}$	$8.3x10^{18}$	$4x10^{19}$	
Workfunction (eV)	4.5					5
Electron charge transfer velocity (cm/s)	10^1					10^{10}
Hole charge transfer velocity (cm/s)	10^{10}					10^1

Table T1
SCAPS simulation software data used to generate electronic band structure of *n*-WS_2, *p*-WS_2-2.4, *p*-WS_2-6.2 and p^+-WS_2-9.8 semiconductors catalysts at flat band condition including glace carbon electrode (electrode contact) and 0.5 M H_2SO_4 electrolyte (electrolyte contct) data.

Table T2
Summary of the HER activity of WS_2 based electrocatalysts measured at differert scan rate.

S.No.	Catalyst	Electrolyte	Scan rate (mV s^{-1})	Overpotential (mV) @ η_{10} (mA cm^{-2})	References
1.	V SAC@1T-WS_2	0.5M H_2SO_4	5	61	[1]
2.	Te doped WS_2	0.5M H_2SO_4	5	116	[2]
3.	W_2C@WS_2 nanoflowers	0.5M H_2SO_4	10	320	[3]
4.	NiS/WS_2/Ni_3S_4	1M KOH/0.5M H_2SO_4	5	50/60	[4]
5.	MOF-derived CoS_2/WS_2	0.5M H_2SO_4	5	79	[5]
6.	Ag/MCNT/WS_2	1M KOH/0.5M H_2SO_4	5	218.9/182	[6]
7.	WS_2@Co_9S_8	1M KOH	5	274	[7]
8.	1 T-Co_4S_3-WS_2/CC	1M KOH	5	75	[8]
9.	CeO_2/WS_2/CC	0.5M H_2SO_4	2	128	[9]
10.	MoS_2/WS_2-rGO	1M KOH	10	118	[10]
11.	Fe_xS_y/WS_2	0.5 M H_2SO_4	5	118	[11]
12.	SA-Ru-MoS_2	1M KOH	2	76	[12]
13.	WS_2/WSe_2	0.5 M H_2SO_4	5	121	[13]
14.	N-WS_2-CC-60	1M KOH/0.5M H_2SO_4	5	175/170	[14]
15.	1T-CoWS/HMCS	0.5 M H_2SO_4	5	25	[15]
16.	CoS_2@WS_2/CC	0.5 M H_2SO_4	0.5	97.2	[16]
17.	Phosphorus doped WS_2	0.5 M H_2SO_4	5	88	[17]
18.	Co-WS_2	0.5 M H_2SO_4	5	255	[18]
19.	400WS/CC	0.5 M H_2SO_4/1M KOH	5	178/235	[19]
20.	1 T-WS2|P-5	0.5 M H_2SO_4/1M KOH	5	125/190	[20]
21.	5% Co-WS_2	0.5 M H_2SO_4/0.5M KOH	10	321/337	[21]
22.	p^+-WS_2-9.8	0.5 M H_2SO_4/1M KOH /1M Na_2SO_4	20	92/248/548	This work

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