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

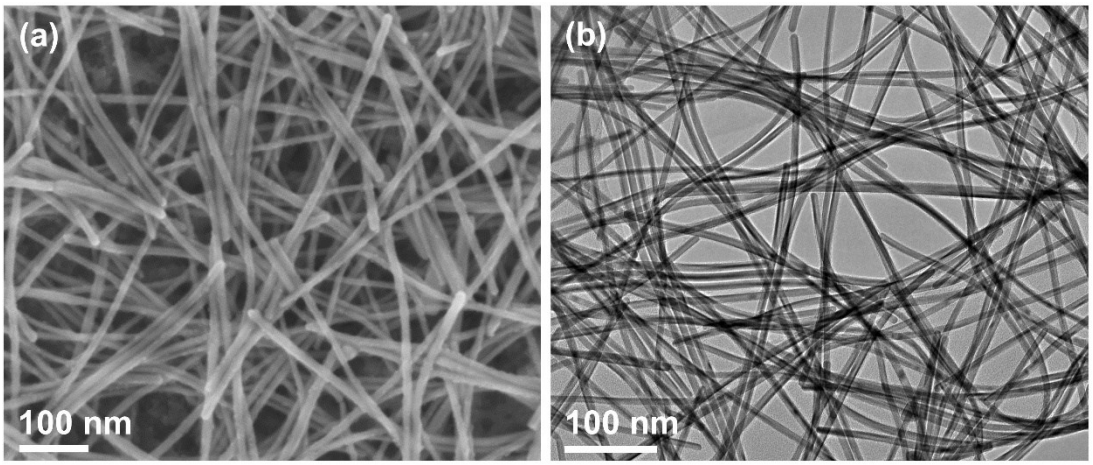

Fig. S1 (a) SEM and (b) TEM images of Pd NWs.

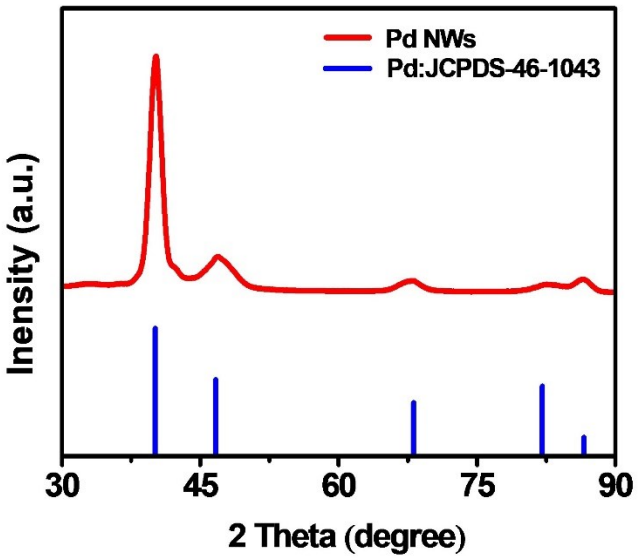

Fig. S2 XRD pattern of the Pd NWs.

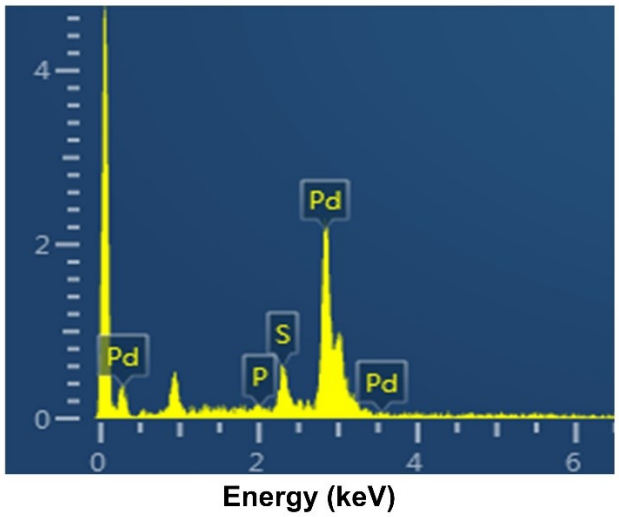

Fig. S3 EDX spectrum of P-Pd_4S NWs.

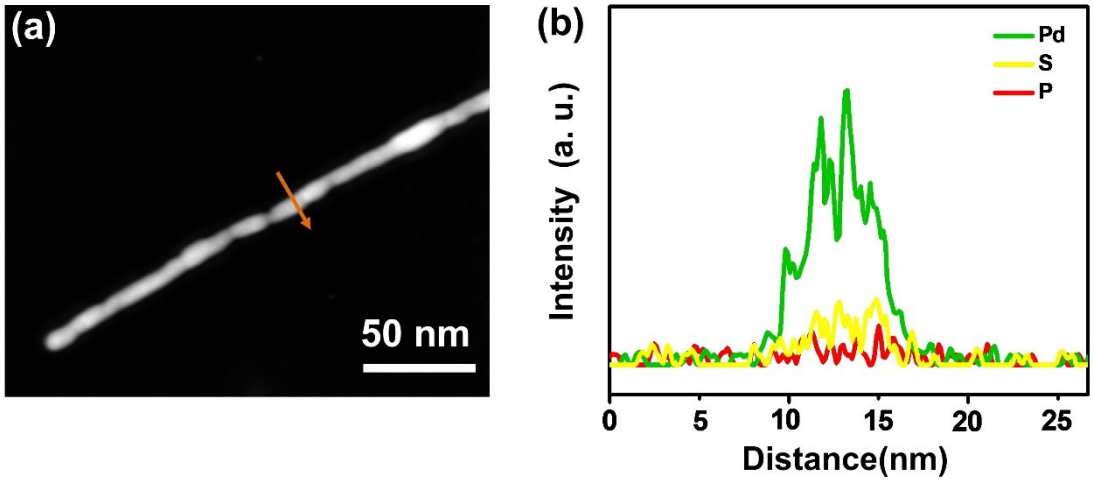

Fig. S4 (a) HAADF-STEM image and (b) corresponding EDX line scanning profile of P-Pd_4S NWs.

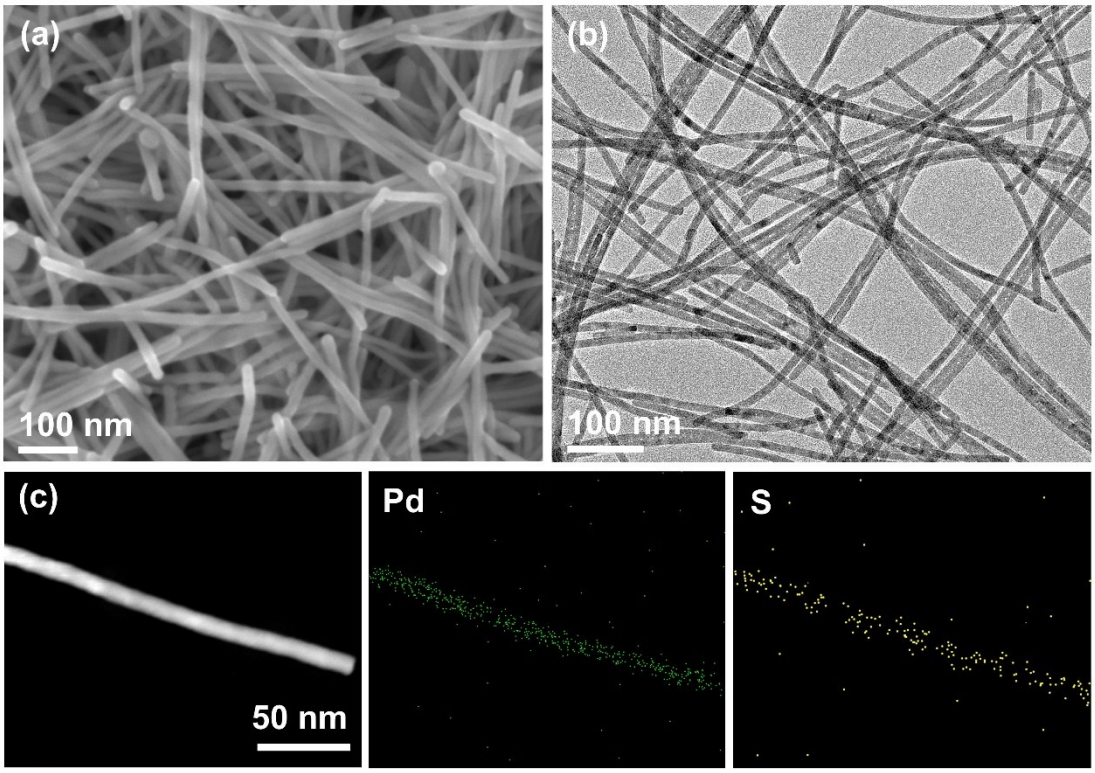

Fig. S5 (a) SEM image, (b) TEM image, (c) HAADF-STEM image and the corresponding elemental mapping of the Pd_4S NWs.

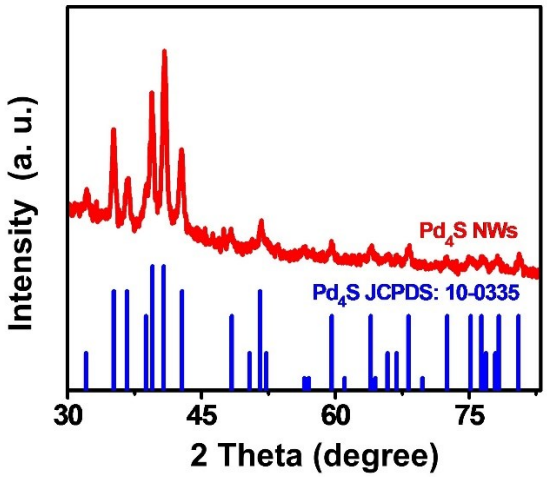

Fig. S6 XRD pattern of the Pd_4S NWs.

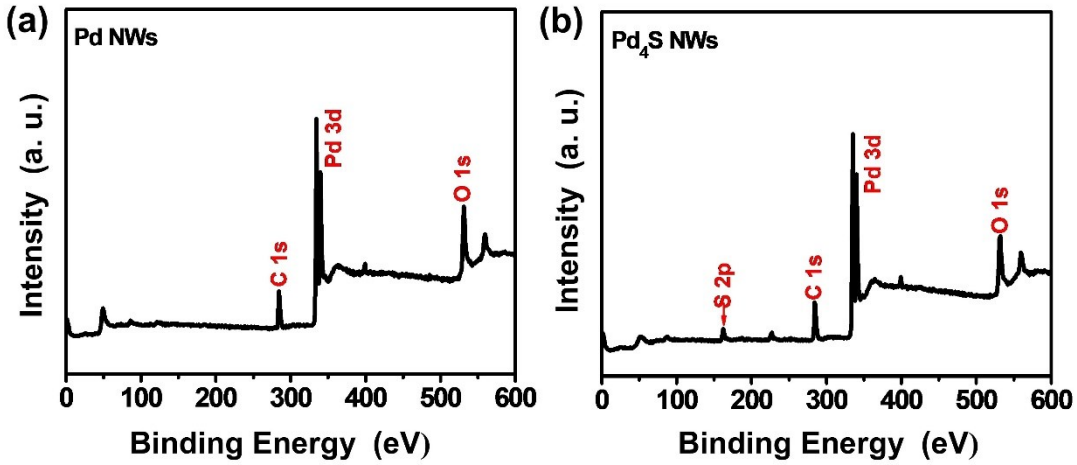

Fig. S7 XPS survey spectra of the Pd NWs (a) and Pd_4S NWs (b).

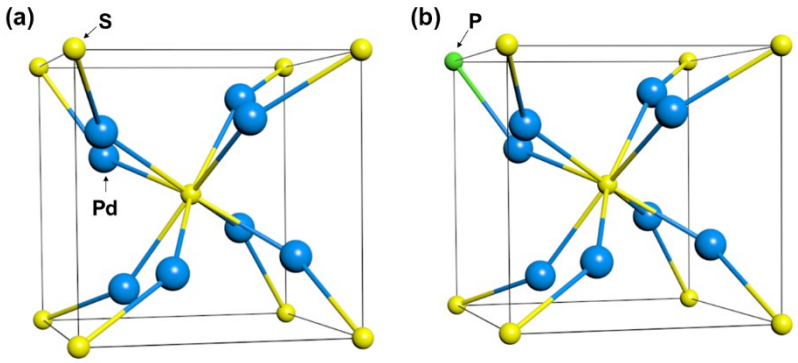

Fig. S8 The unit cells of (a)Pd_4S and (b)P-Pd_4S.

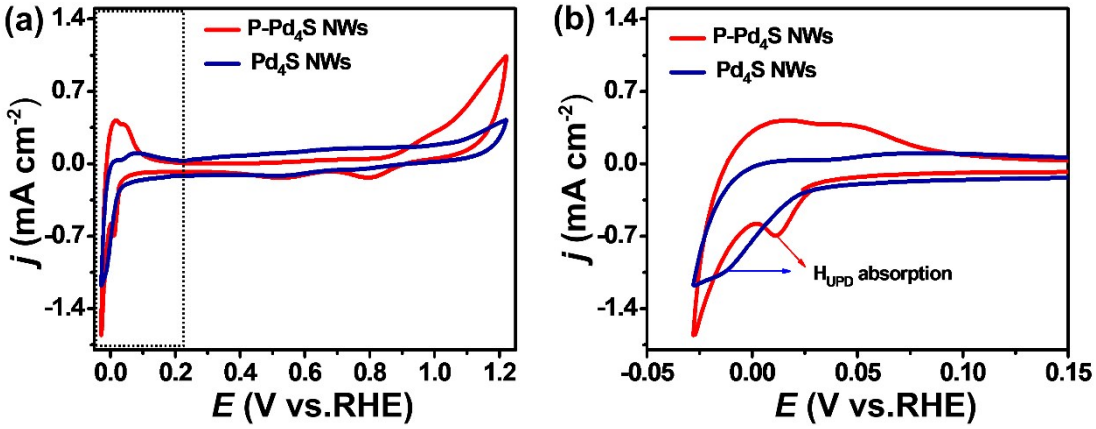

Fig. S9 (a) CV curves for the Pd_4S NWs and P-Pd_4S NWs recorded in 0.5 M H_2SO_4 with a scan rate of 50 mV s^{-1}. (b) The regions between -0.05 and 0.15 V from (a).

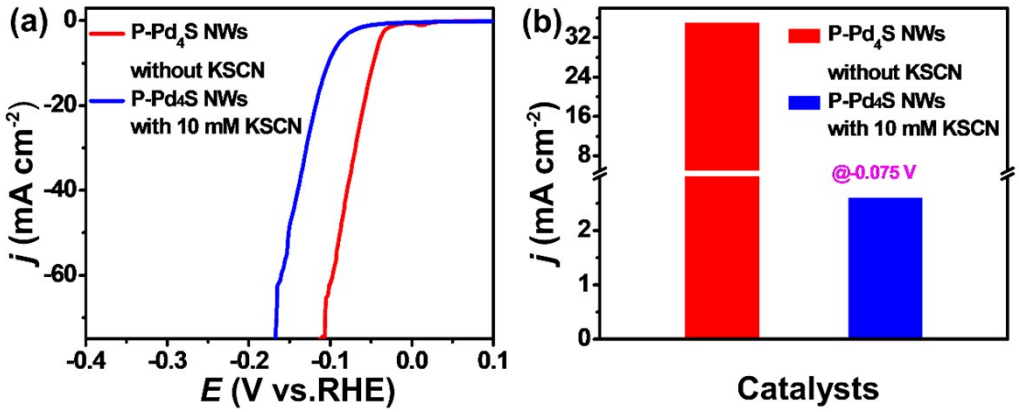

Fig. S10 (a) LSV HER curves of the P-Pd_4S NWs with or without 10 mM KSCN in 0.5 M H_2SO_4. (b) The comparison of the cathodic current densities of the P-Pd_4S NWs with or without 10 mM KSCN in 0.5 M H_2SO_4 at -0.075 V (vs. RHE).

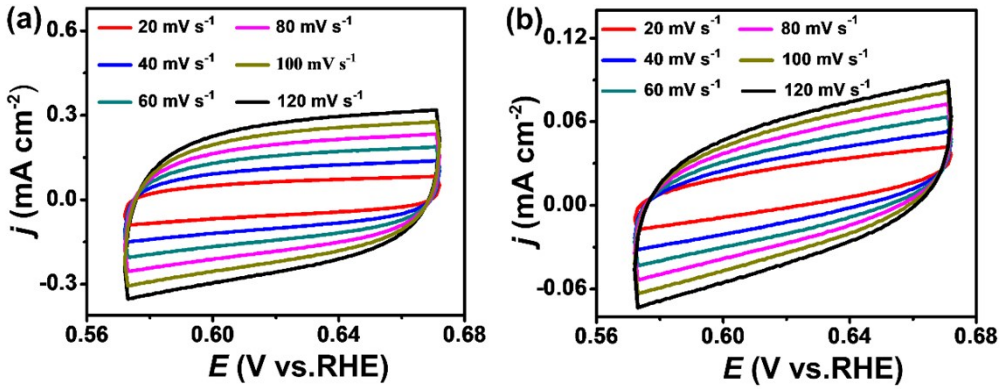

Fig. S11 CV curves with different scan rates for P-Pd_4S NWs (a) and Pd_4S NWs (b).

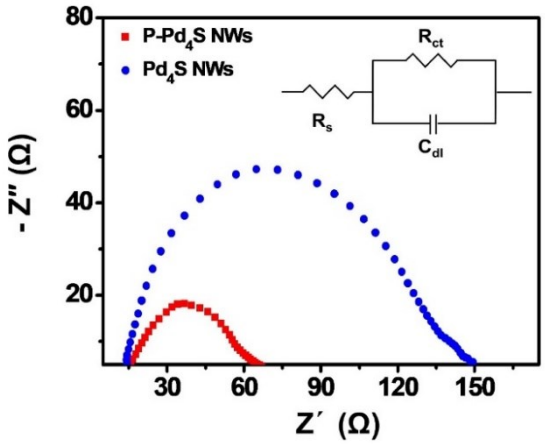

Fig. S12 Electrochemical impedance spectra (EIS) of P-Pd_4S NWs and Pd_4S NWs at 300 mV overpotential.

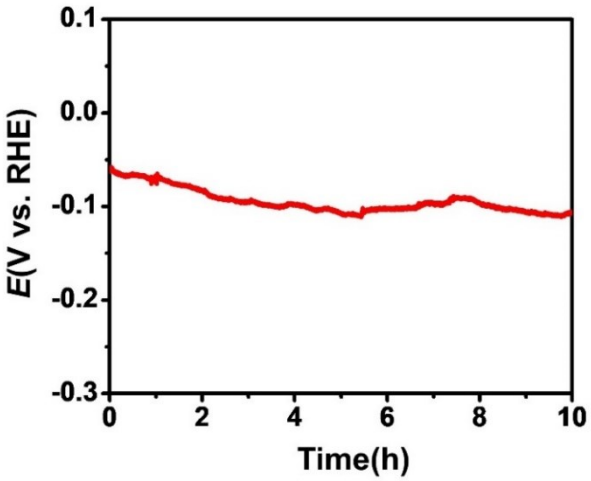

Fig. S13 V-t curve recorded at a current of 10 mA cm^{-2} for Pt/C.

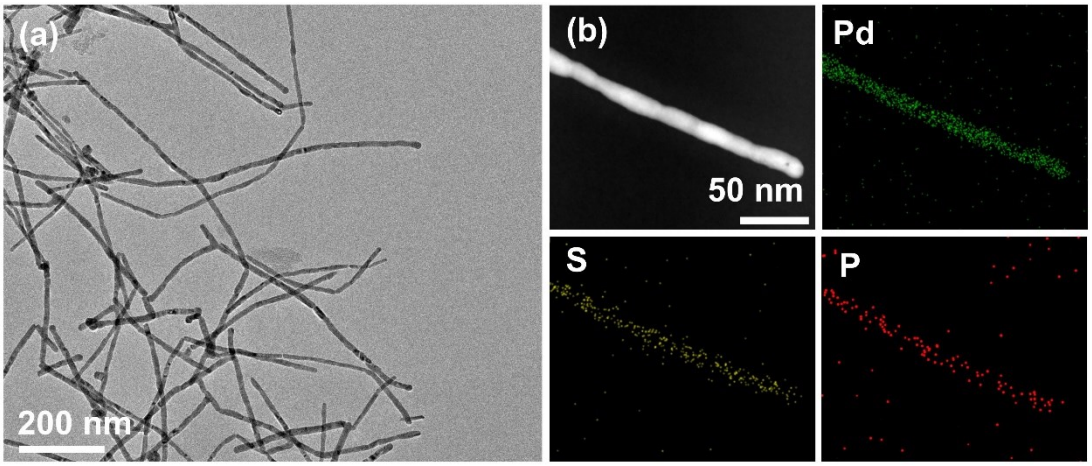

Fig. S14 (a) TEM image and (b) HAADF-STEM and the corresponding elemental mapping of the P-Pd_4S NWs after HER stability testing.

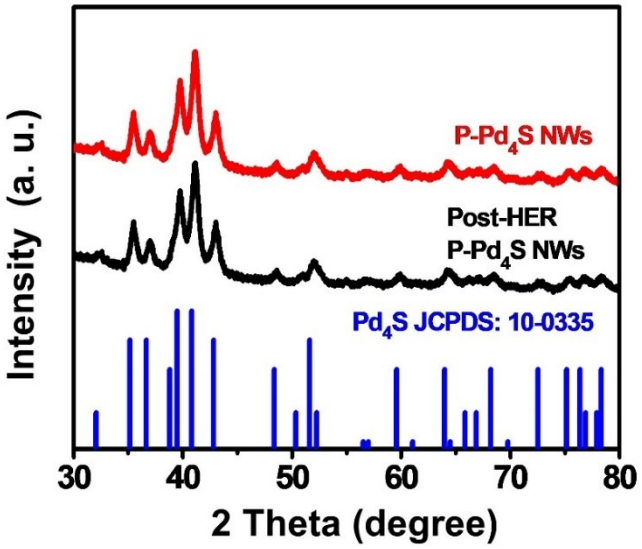

Fig. S15 XRD patterns of the fresh and post-HER P-Pd_4S NWs.

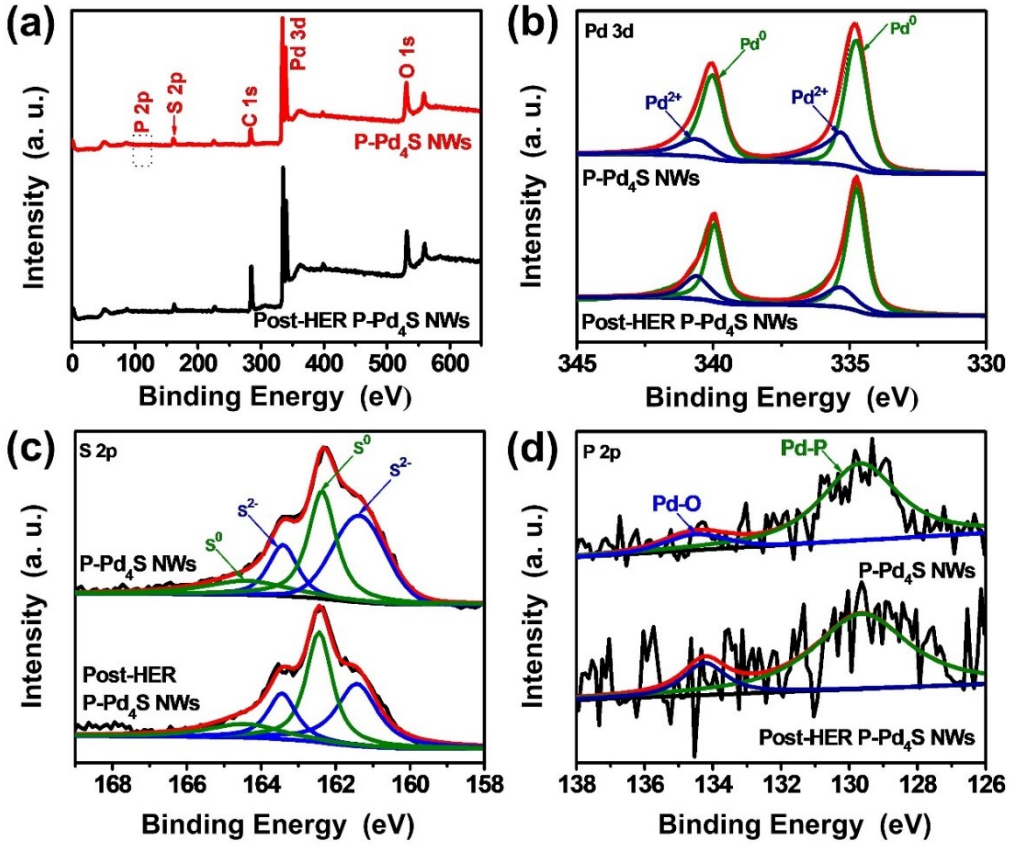

Fig. S16 (a) XPS survey spectra, (b) high-resolution Pd 3d XPS spectra, (c) high-resolution S 2p XPS spectra, (d) high-resolution P 2p spectra of the fresh and post-HER P-Pd_4S NWs.

Table S1. Comparison of HER activity for the P-Pd_4S NWs and some other reported non-Pt-based electrocatalysts.

Catalyst	Overpotential at -10 mA cm^{-2} (mV)	Tafel slop (mV dec^{-1})	Electrolyte	Ref.
P-Pd_4S NWs	**47**	**32.7**	**0.5 M H_2SO_4**	**This work**
$Ni_{1.4}(Fe_{0.6})P@Al_2O_3$	53	38	0.5 M H_2SO_4	[1]
$Rh_3Pb_2S_2$/C	87.3	45.6	0.5 M H_2SO_4	[2]
MoP@NCF	121.8	627	0.5 M H_2SO_4	[3]
Ru_2P nanoparticles	55	34.1	0.5 M H_2SO_4	[4]
P-$CoTe_2$/C nanoparticles	159	64.62	0.5 M H_2SO_4	[5]
$Pd_3P_2S_8$	52	29	0.5 M H_2SO_4	[6]
P-Fe_3O_4@3DG	65	50.2	0.5 M H_2SO_4	[7]
P-MoS_2	118	52	0.5 M H_2SO_4	[8]
MoC_x/C	50	62	0.5 M H_2SO_4	[9]
CoP/NPC/TF	91	54	0.5 M H_2SO_4	[10]
$Ni_3(VO4)_2$	90	50	0.5 M H_2SO_4	[11]
MoP@NC	135	57	0.5 M H_2SO_4	[12]
CoP/NiCoP	60	64	0.5 M H_2SO_4	[13]
Pd-CoS_2-MoS_2/C-600	144	59.9	0.5 M H_2SO_4	[14]
Al–NiP_2 NSs/CFP	58	46	0.5 M H_2SO_4	[15]

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