Sodium Tungsten Bronze-Supported Pt Electrocatalysts for High-Performance Hydrogen Evolution Reaction

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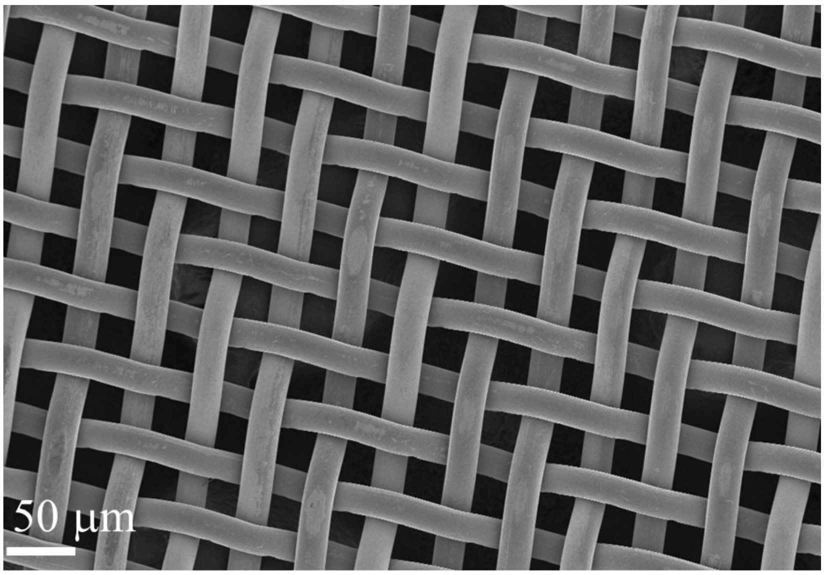

Figure S1. FESEM image of the bare SM.

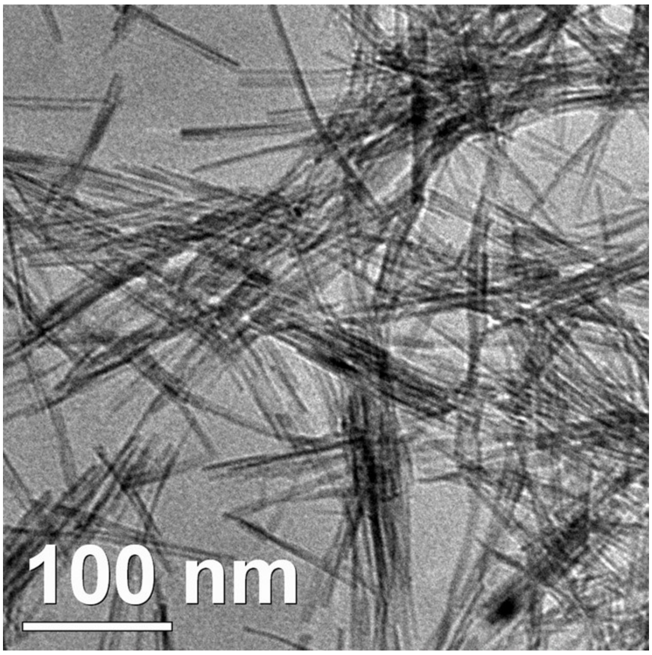

Figure S2. TEM image of Na_xWO_3 nanotube.

It is difficult to observe the nanotube-like morphology of Na_xWO_3 bundle due to the aggregation, we can indirectly investigate its morphology. After ultrasonic treatment for 5 h, the Na_xWO_3 bundle can be disassembled to single Na_xWO_3 nanotube as shown in Figure S2.

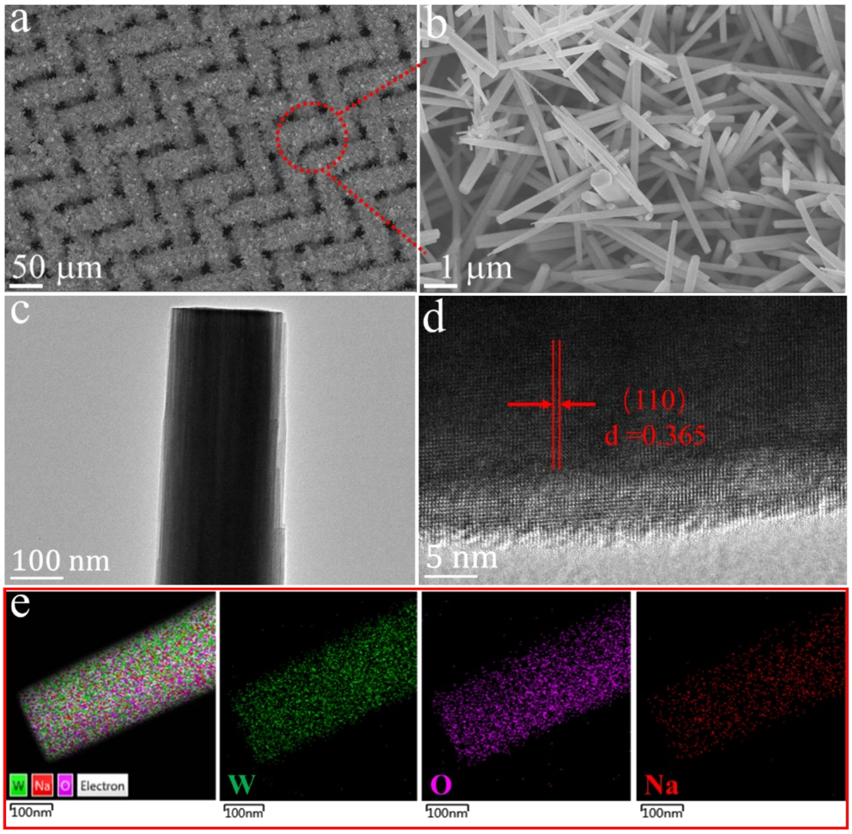

Figure S3. (a,b) FESEM images of R-Na_xWO_3 with different magnifications, (c,d) TEM and HRTEM of R-Na_xWO_3 nanotube bundles. (e) The corresponding EDX mappings for W, O, and Na, respectively.

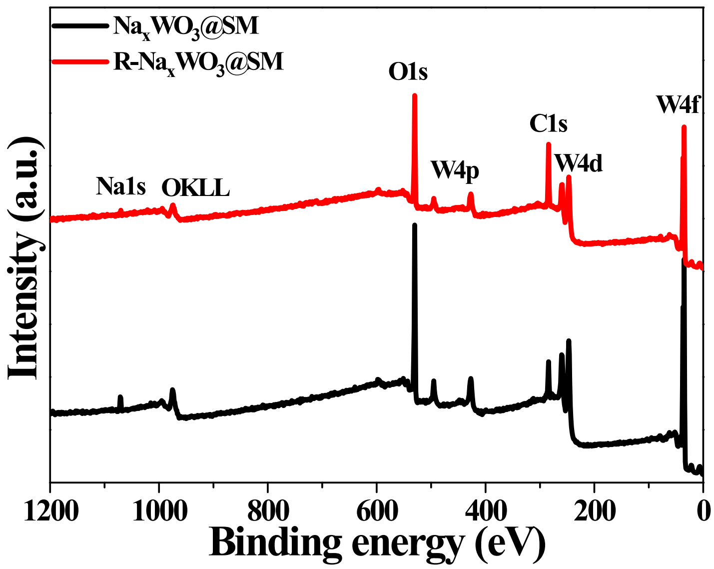

Figure S4. XPS survey of Na_xWO_3@SM and R-Na_xWO_3@SM

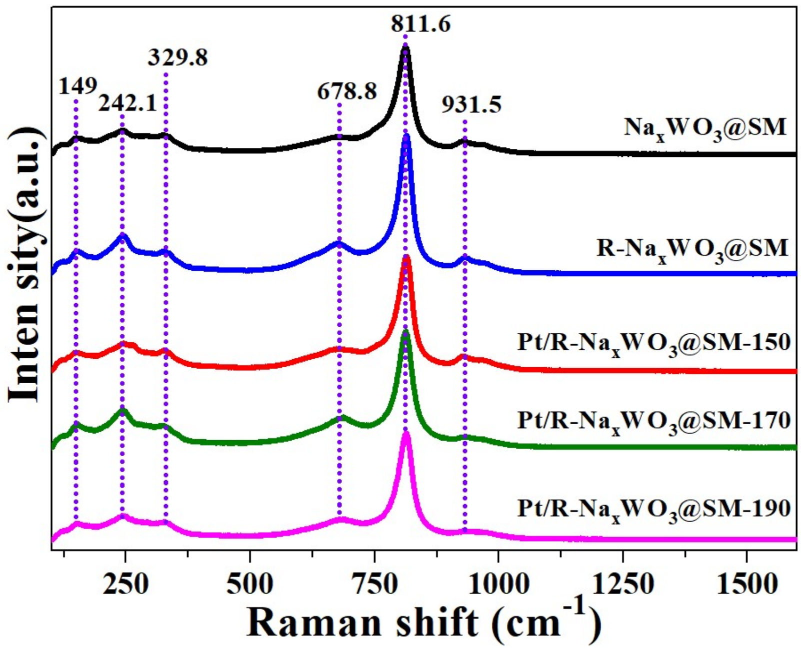

Figure S5. Raman spectra of Na_xWO_3@SM, R-Na_xWO_3@SM, Pt/R-Na_xWO_3@SM-150, Pt/R- Na_xWO_3@SM-170, and Pt/R- Na_xWO_3@SM-190.

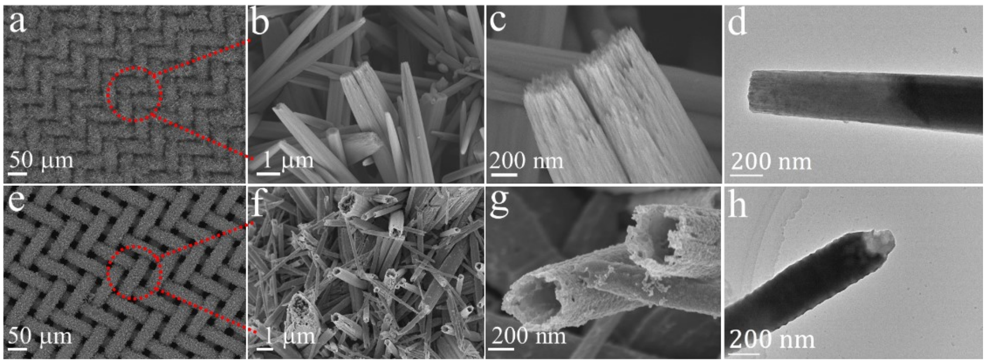

Figure S6. (a-c) FESEM images and (d) TEM image of Pt/R-Na_xWO_3@SM-150. (e-g) FESEM images and (h) TEM image of Pt/R-Na_xWO_3@SM-190.

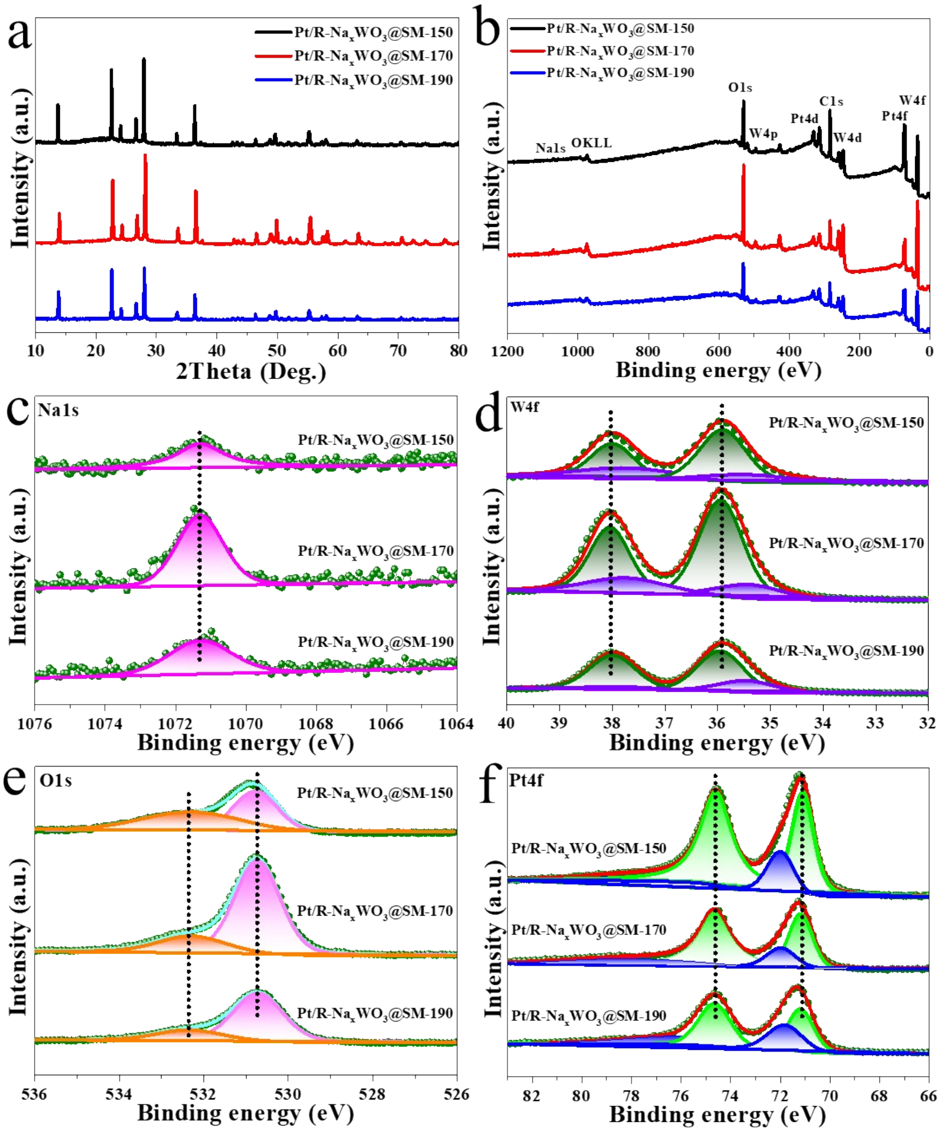

Figure S7. XRD pattern (a), XPS spectra (b), Na1s spectra (c), W4f spectra (d), O1s spectra (e), and Pt4f spectra (f) of Pt/R-Na_xWO_3@SM-150, Pt/R-Na_xWO_3@SM-170, and Pt/R-Na_xWO_3@SM-170, respectively.

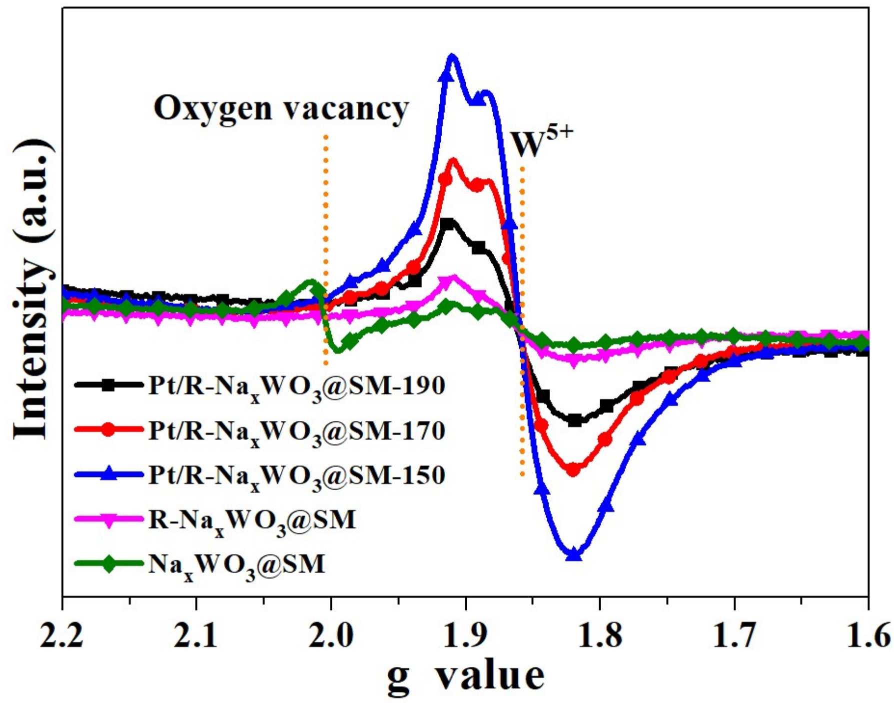

Figure S8. EPR spectra of Pt/R-Na_xWO_3@SM-190, Pt/R-Na_xWO_3@SM-170, Pt/R-Na_xWO_3@SM-150, R-Na_xWO_3@SM, and Na_xWO_3@SM, respectively.

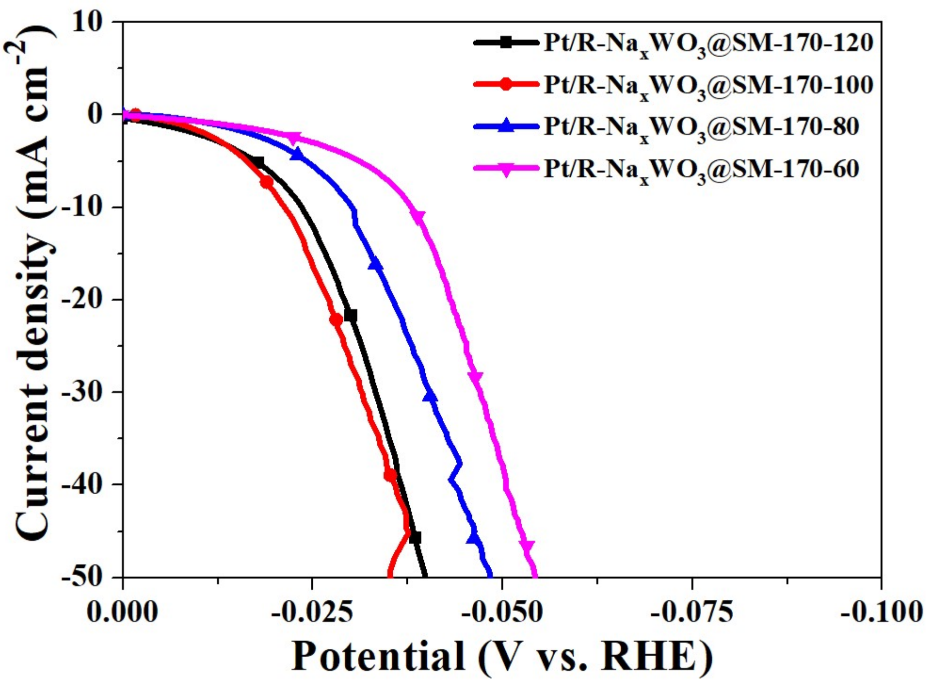

Figure S9. LSV curves of Pt/R-Na_xWO_3@SM-170-120, Pt/R-Na_xWO_3@SM-170-100, Pt/R-Na_xWO_3@SM-170-80, and Pt/R-Na_xWO_3@SM-170-60.

For optimizing the loading amount of Pt on the surface of R-Na_xWO_3, control experiments were carried out by changing the volume of chloroplatinic acid with 120 μL, 100 μL, 80 μL, and 60 μL under the same operating condition, the as-synthesized samples are defined as Pt/R-Na_xWO_3@SM-170-120, Pt/R-Na_xWO_3@SM-170-100, Pt/R-Na_xWO_3@SM-170-80, and Pt/R-Na_xWO_3@SM-170-60, respectively.

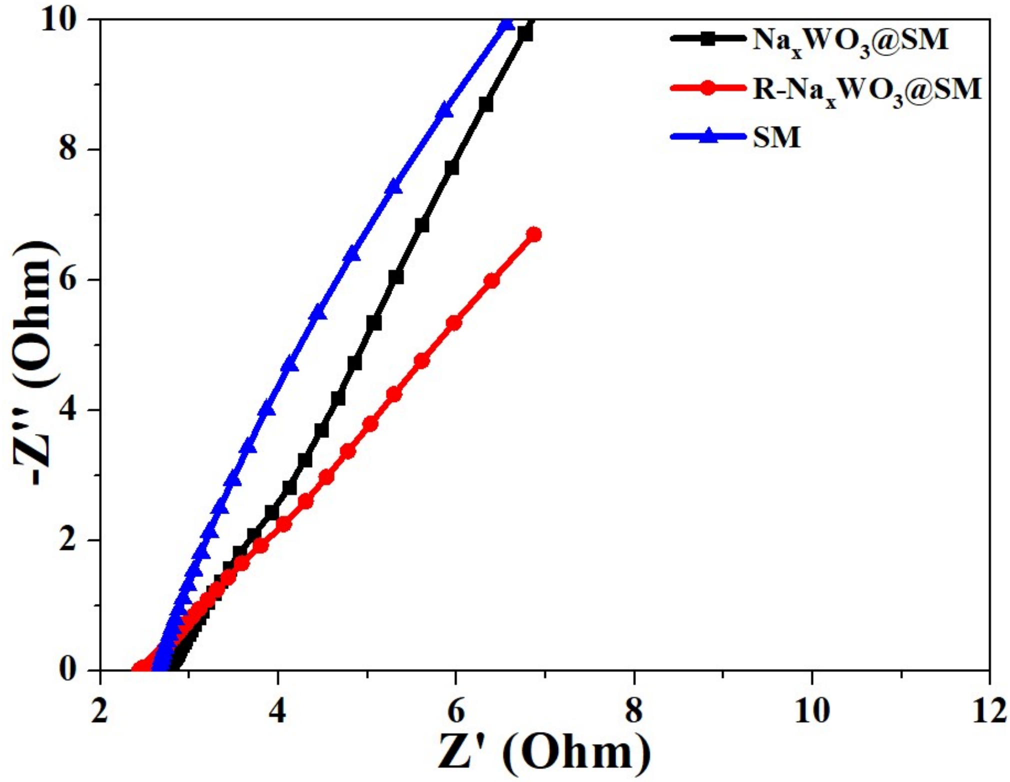

Figure S10. Electrochemical impedance plots for SM, R-Na_xWO_3@SM, and Na_xWO_3@SM.

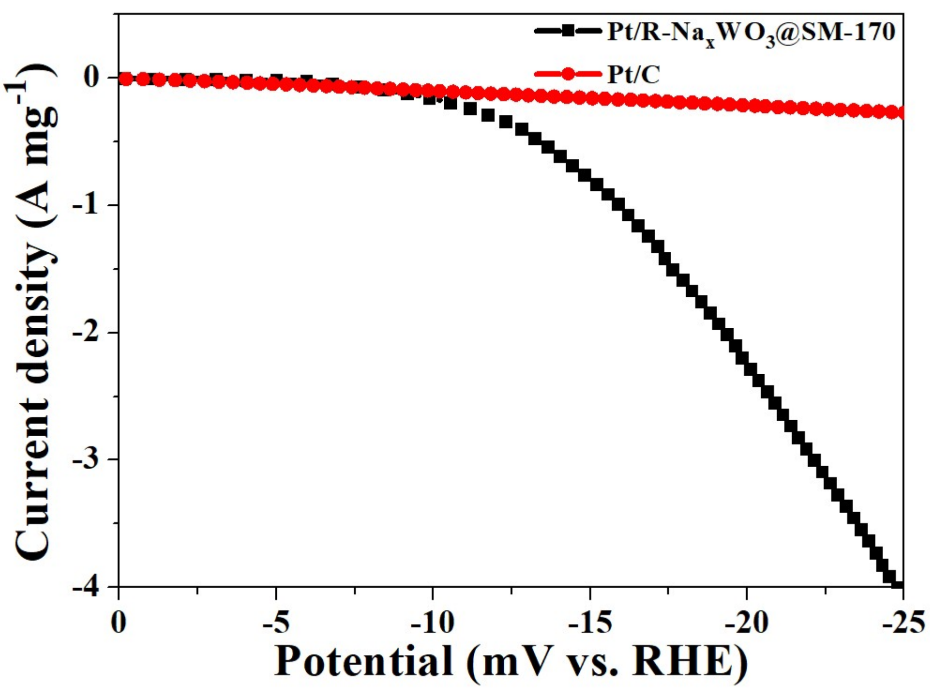

Figure S11. The polarization curves for Pt/R-Na_xWO_3@SM-170 and Pt/C in 0.5 M H_2SO_4 with a scan rate of 2 mV s^{-1}.

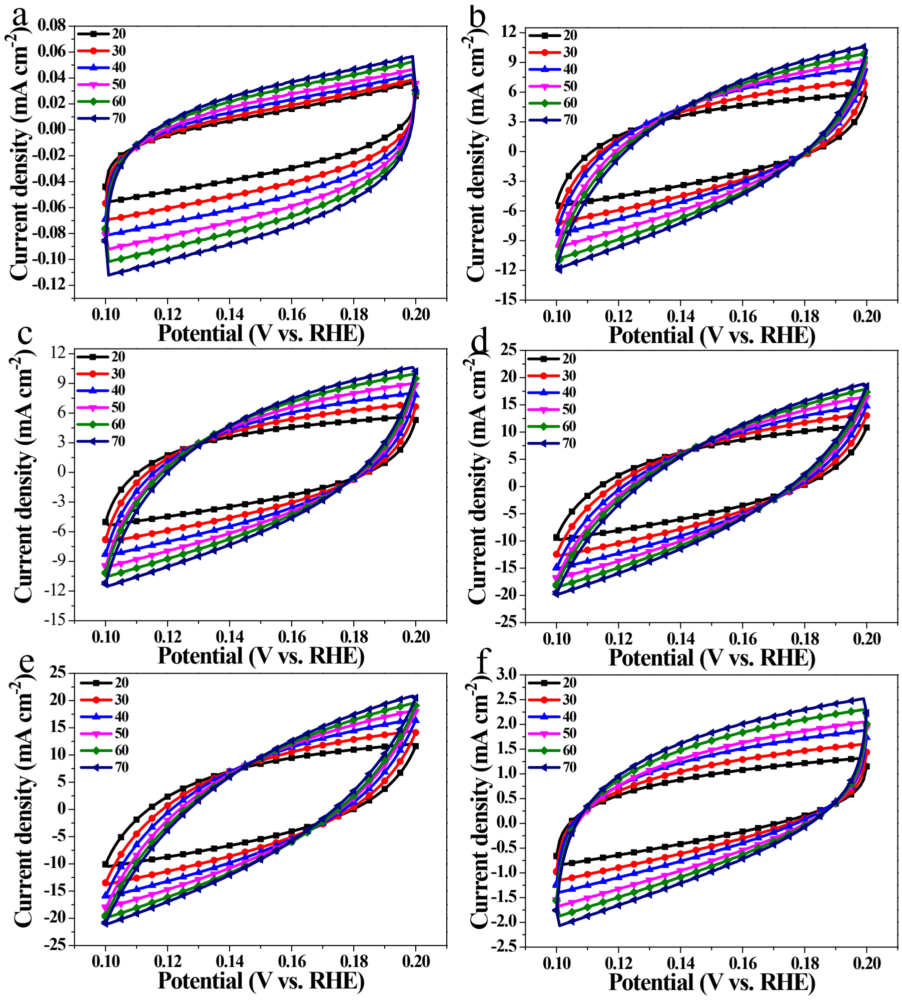

Figure S12. Cyclic voltammograms of (a) SM, (b) Na_xWO_3@SM, (c) R-Na_xWO_3@SM, (d) Pt/R-Na_xWO_3@SM-150, (d) Pt/R-Na_xWO_3@SM-170, and (e) Pt/R-Na_xWO_3@SM-190 samples in the non-faradaic capacitance current range at scan rates of 20, 30, 40, 50, 60, and 70 mV s^{-1}.

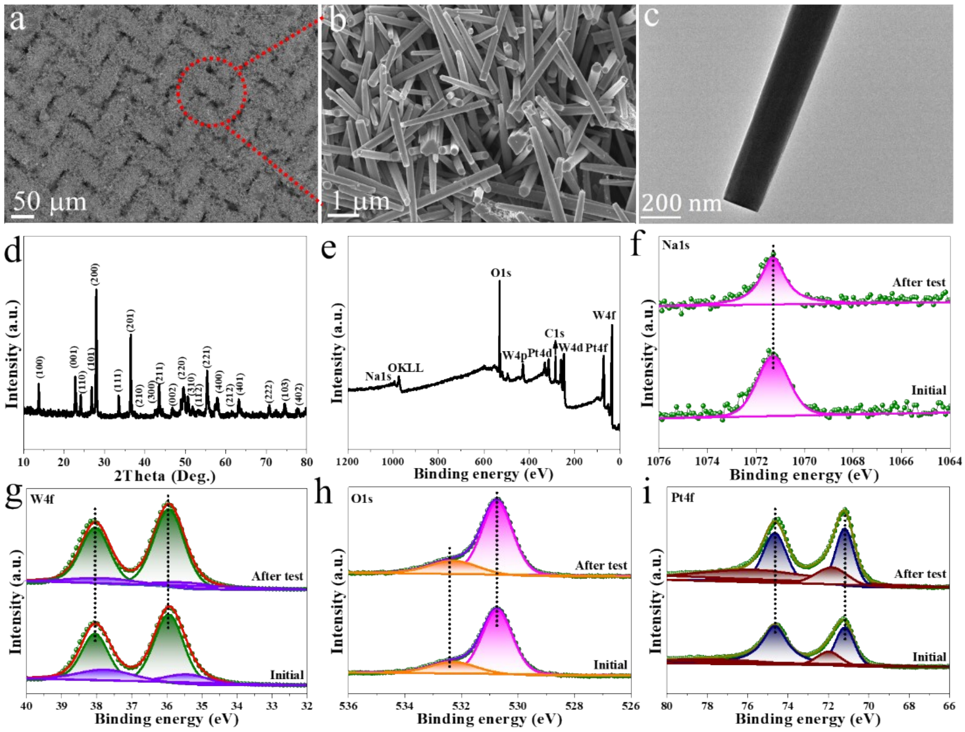

Figure S13. (a,b) FESEM images and (c) TEM image of Pt/R-Na_xWO_3@SM-170 after HER for 25 h. (d,e) XRD pattern and XPS spectra of Pt/R-Na_xWO_3@SM-170 after HER for 25 h. (f) Na1s spectra, (g) W4f spectra, (h) O1s spectra, and (i) Pt4f spectra of Pt/R-Na_xWO_3@SM-170 before and after stability test.

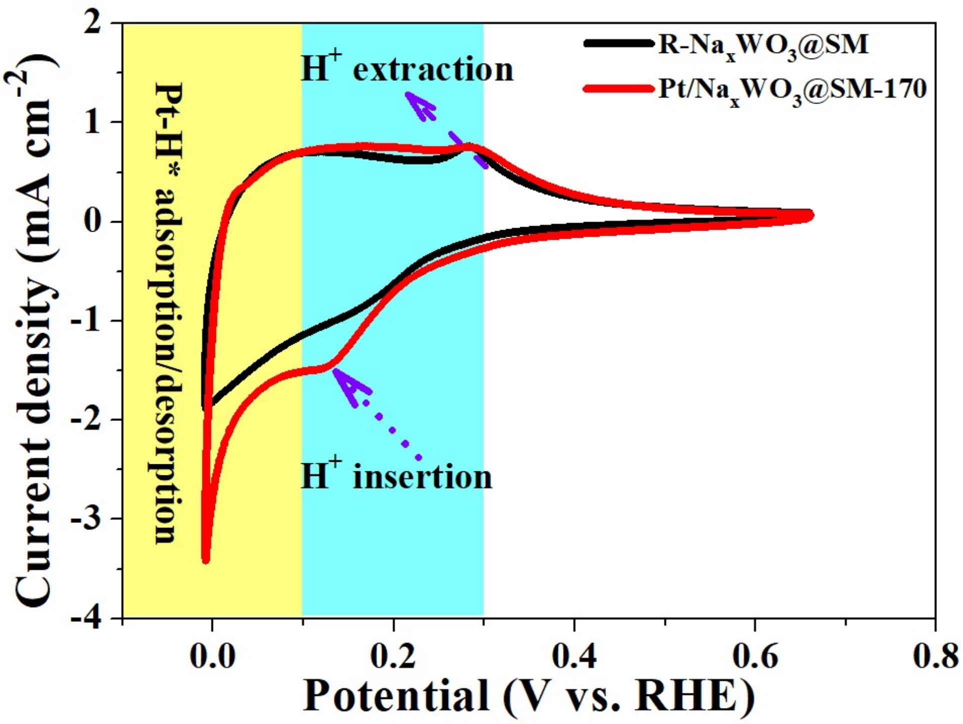

Figure S14. CV curves of Pt/R-Na_xWO_3@SM-170 and R-Na_xWO_3@SM at a scanning rate of 2 mV s^{-1}.

Table S1. The ratio of W^{5+}/W^{6+} in Pt/R-Na_xWO_3@SM-150, Pt/R-Na_xWO_3@SM-170, and Pt/R-Na_xWO_3@SM-190.

	Pt/R-Na_xWO_3@SM-150	**Pt/R-Na_xWO_3@SM-170**	**Pt/R-Na_xWO_3@SM-190**
W^{5+}/W^{6+}	37.7%	30.3%	23.7%

Table S2. Electrocatalytic HER parameters of Pt/R-Na_xWO_3@SM-170 fabricated in this work and Pt-based catalysts reported previously at 10 mA cm^{-2} in 0.5 M H_2SO_4.

Catalysts	**Overpotential (mV)**	**Tafel slope (mV dec^{-1})**	**References**
Pt/R-Na_xWO_3@SM-170	20	18.6	This work
Pt-SA/ML-WO_3-300	25	27	[1]

Pt/WO_3	39	32.3	[2]
$Pt\text{-}MoS_2$	50	40	[3]
$Pt\text{-}SA/m\text{-}WO_{3-x}$	47	45	[4]
Pt_1/MoO_3	23.3	28.8	[5]
$Pt\text{-}SA/\alpha\text{-}MoO_x$	19	123	[6]
Pt Cs/MoO_2 NSs	47	33	[7]
PtN_x/TiO_2	67	34	[8]
Pt-PVP/TNR	21	27	[9]
Pt/def-WO_3@CFC	42	61	[10]
EG-Pt/CoP-1.5	21	42.5	[11]
Pt/RuCeO_x-PA	41	31	[12]
PtW_6O_{24}/C	22	29.8	[13]
$Pt/Ti_{0.9}Mo_{0.1}O_2$	26	36	[14]
Pt@Co SAs-ZIF-NC	27	21	[15]
$Pt_{61}La_{39}$@KB	38	29	[16]
Mo_2C@NC@Pt	27	28	[17]
AL-Pt/Pd_3Pb	13.8	18	[18]
Pt/f-MWCNTs	43.9	30	[19]
$CoPt_2$	17	35	[20]
Pt/GNs	25	33	[21]
Pd@PtCu/C	60	26.2	[22]
$Pt_{3.21}Ni$@Ti_3C_2	18.55	13.37	[23]
PtW NPs	19.4	27.8	[24]
Pt–Pd@NPA	28.1	31.2	[25]
Pt@MoS_2/NiS_2	34	40	[26]

Pt/NBF-ReS_2/Mo_2CT_x	29	24	27
PtRu/CC_{1500}	8	25	28
Pt–HNCNT	15	29.1	29
PtCu/CoP	20	28	30
Pt_1/OLC	38	36	31
Ni-MOF@Pt	43	30	32
$PtCNP_2$	22	31.2	33

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