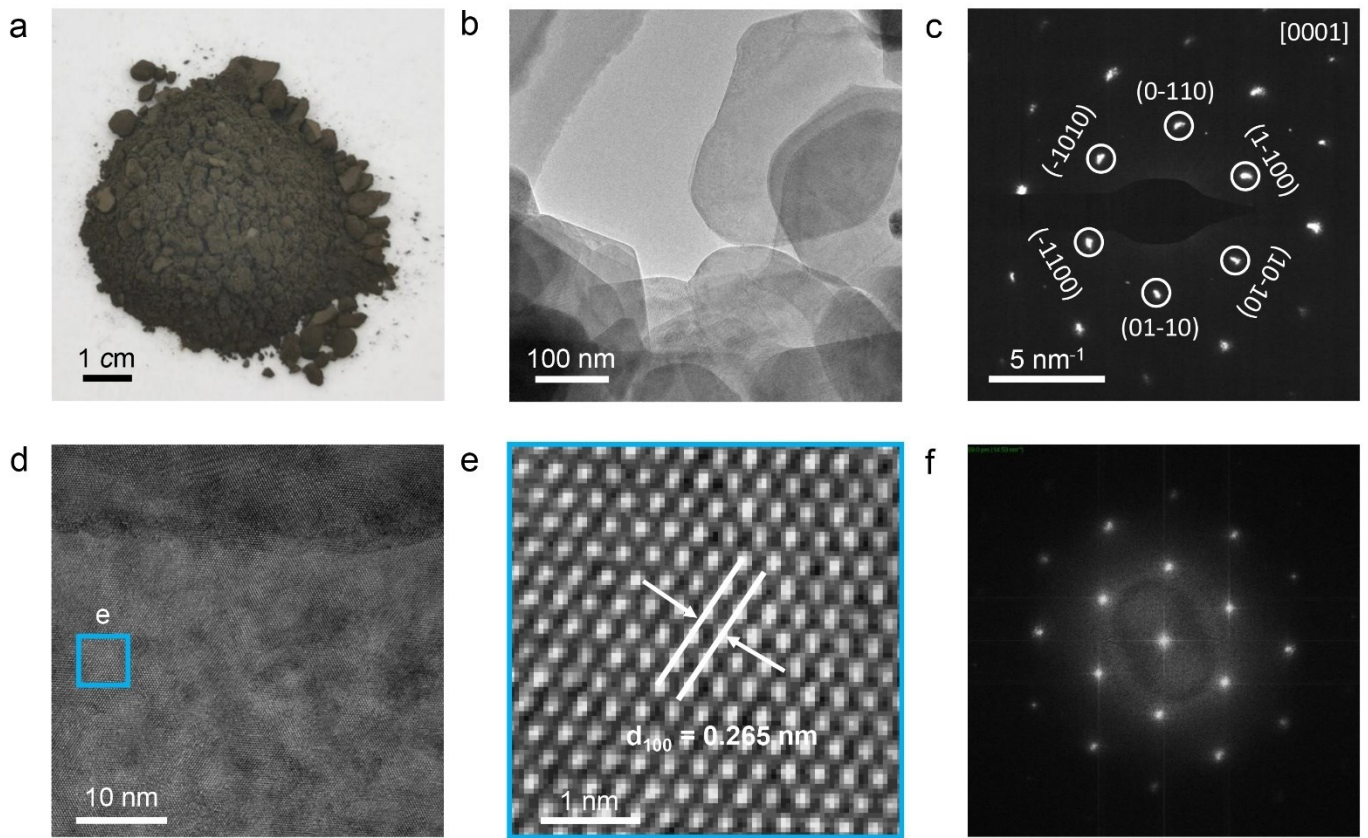


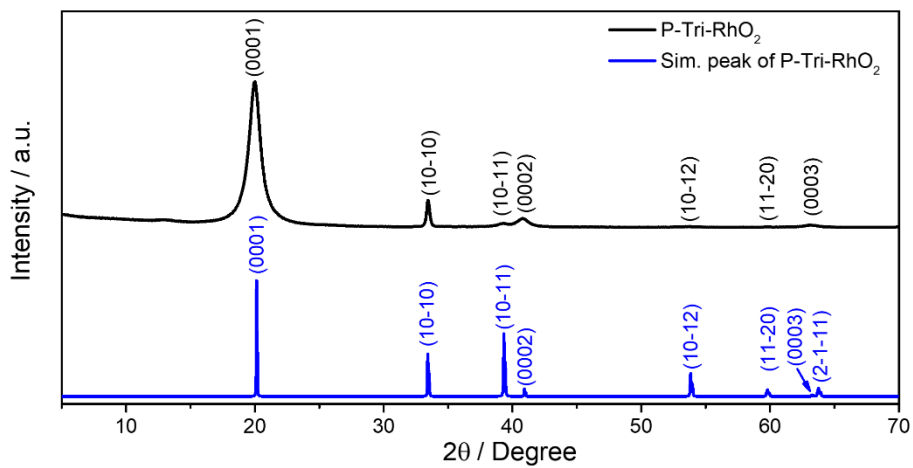
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Supplementary Figure 1. Schematic representation of radio-frequency assisted molten-alkali method. The rhodium (III) chloride (RhCl_3) and potassium hydroxide (KOH) were selected as the raw materials and uniformly mixed in crucible. This figure was made with the Cinema 4D Software.



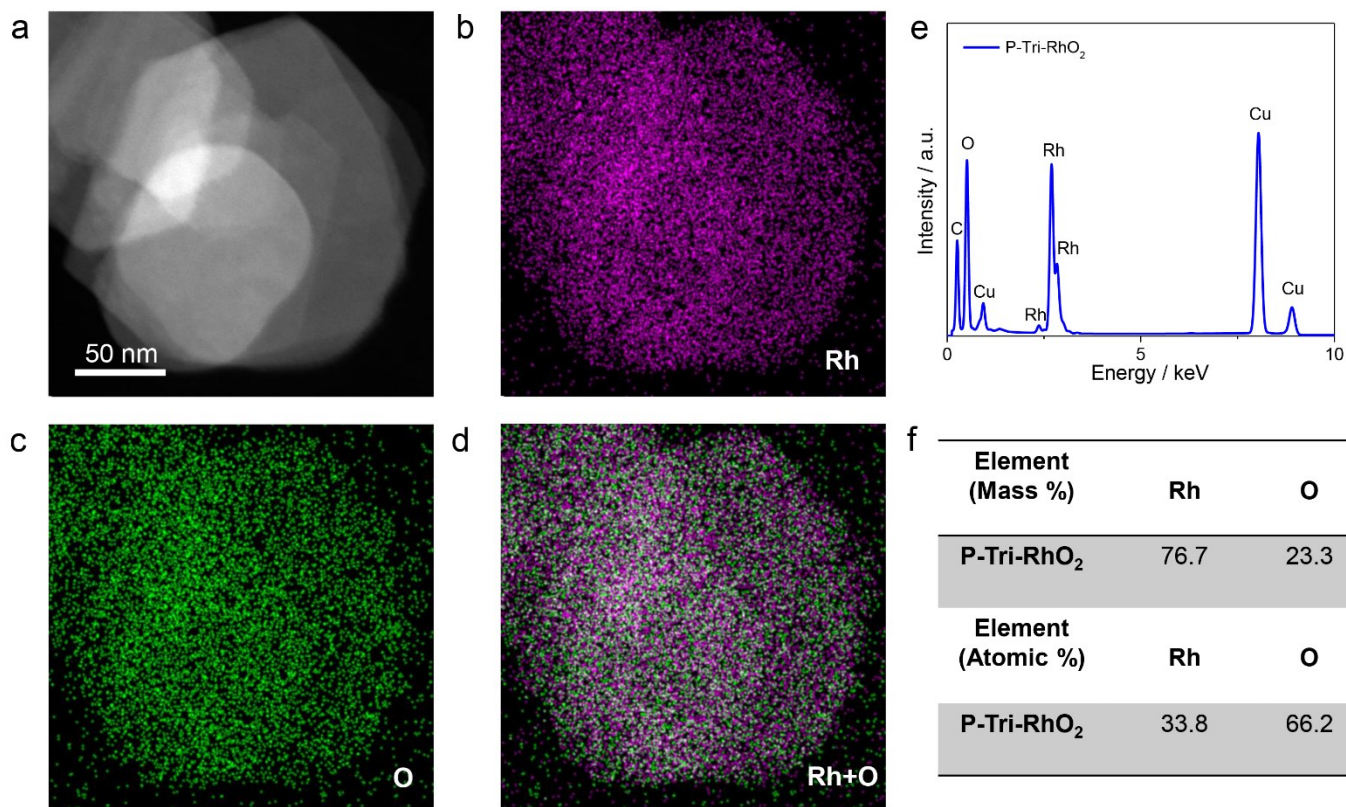
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2 **Supplementary Figure 2. Digital image, SEM, SAED, HRTEM and FFT images of P-Tri-RhO₂.** (a)
 3 The digital image of P-Tri-RhO₂ powder. (b) TEM image and (c) SAED pattern of P-Tri-RhO₂. (d)
 4 HRTEM image and (e) its partially enlarged view. (f) The fast Fourier transform (FFT) from (e).



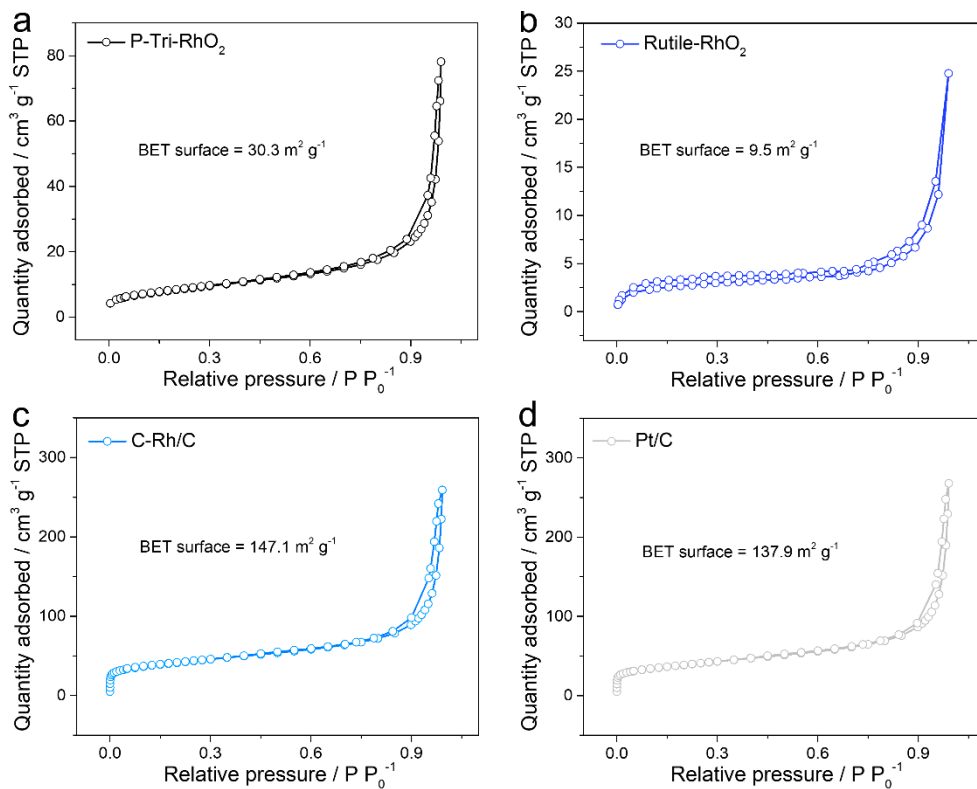
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2 **Supplementary Figure 3. Comparison of XRD pattern and simulated XRD pattern for P-Tri-RhO₂.**
 3 Comparison of XRD patterns of P-Tri-RhO₂ (black curve) and simulated X-ray diffraction peak of
 4 P-Tri-RhO₂ (red curve).
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2 **Supplementary Figure 4. EDX and elemental analysis of P-Tri-RhO₂.** (a-d) EDX-mapping images of
 3 P-Tri-RhO₂, where Rh and O are uniformly distributed in the nanosheet structure. (e) EDX analysis of
 4 P-Tri-RhO₂. (f) The table of the mass and atomic ratios of Rh to O in P-Tri-RhO₂ by elemental analysis
 5 method (elementar EL III).

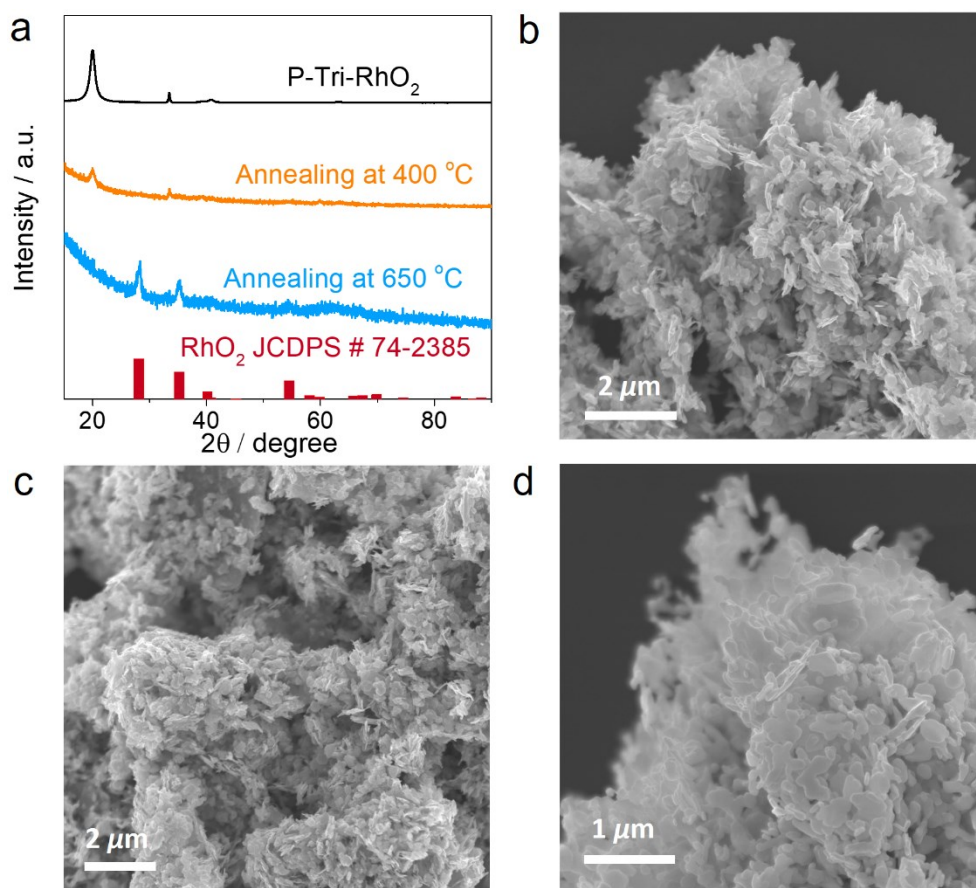


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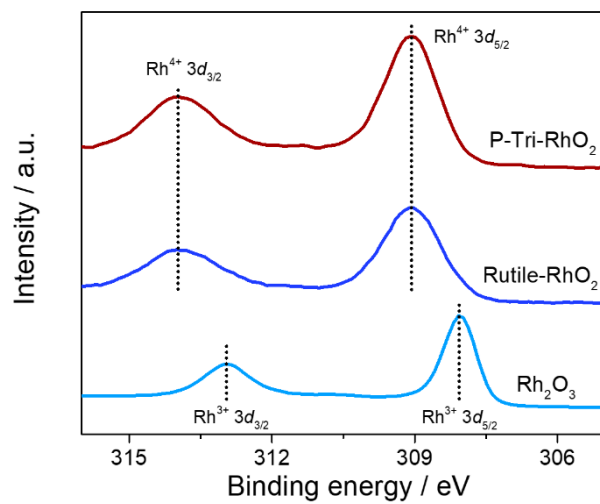
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Supplementary Figure 5. BET surface area measurements for different catalysts. BET surface area measurements for (a) P-Tri-RhO₂, (b) Rutile-RhO₂, (c) C-Rh/C and (d) Pt/C.

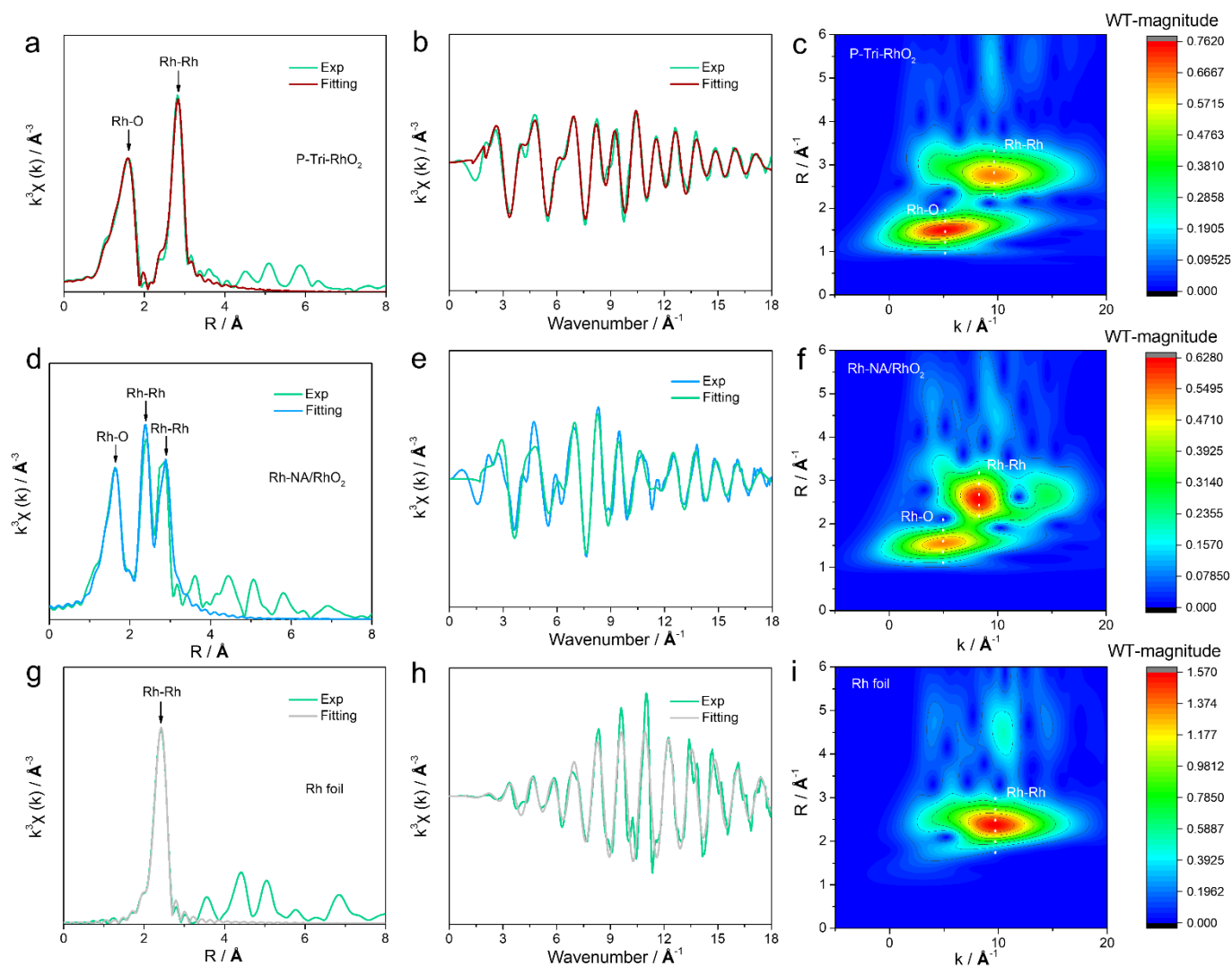


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2 **Supplementary Figure 6. XRD patterns and SEM images obtained by annealing P-Tri-RhO₂ at**
3 **different temperatures.** (a) Temperature-dependent XRD patterns of annealing P-Tri-RhO₂ at different
4 temperatures. The corresponding SEM images of (b) P-Tri-RhO₂ and the products by annealing
5 P-Tri-RhO₂ at (c) 400 °C and (d) 650 °C.



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2 **Supplementary Figure 7. XPS measurements for different samples.** XPS spectra of Rh 3d peaks for
3 P-Tri-RhO₂, Rutile-RhO₂ and Rh₂O₃.



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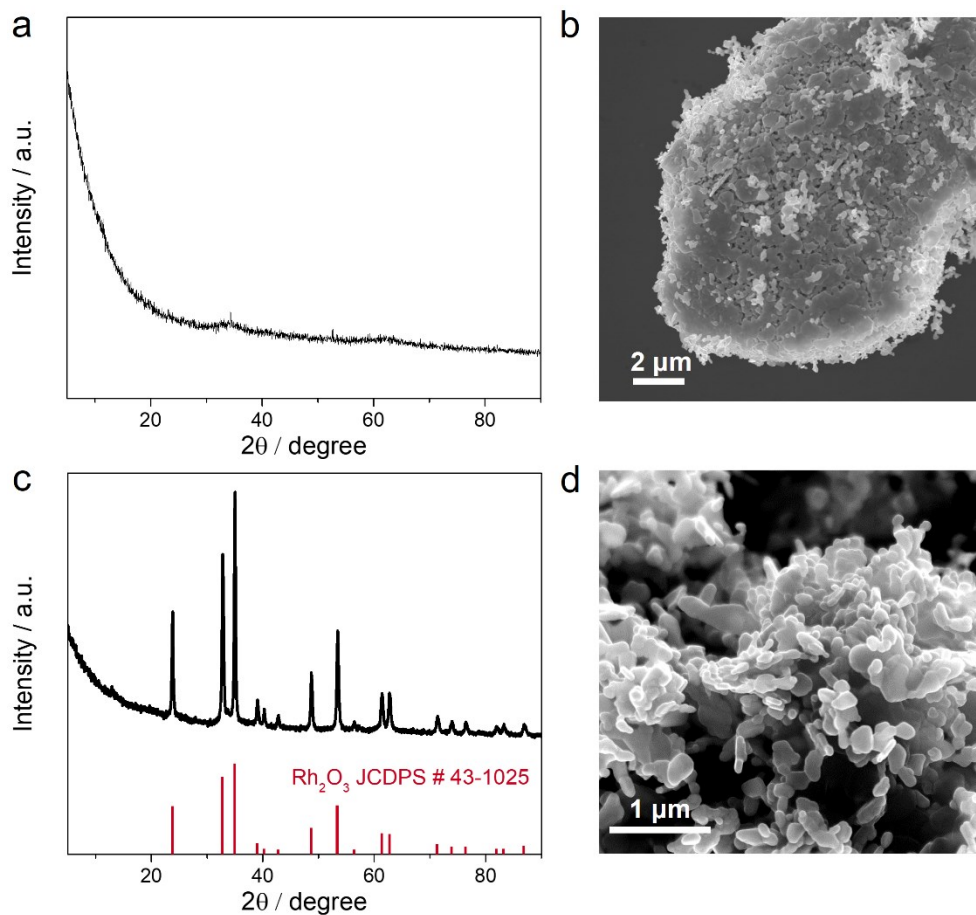
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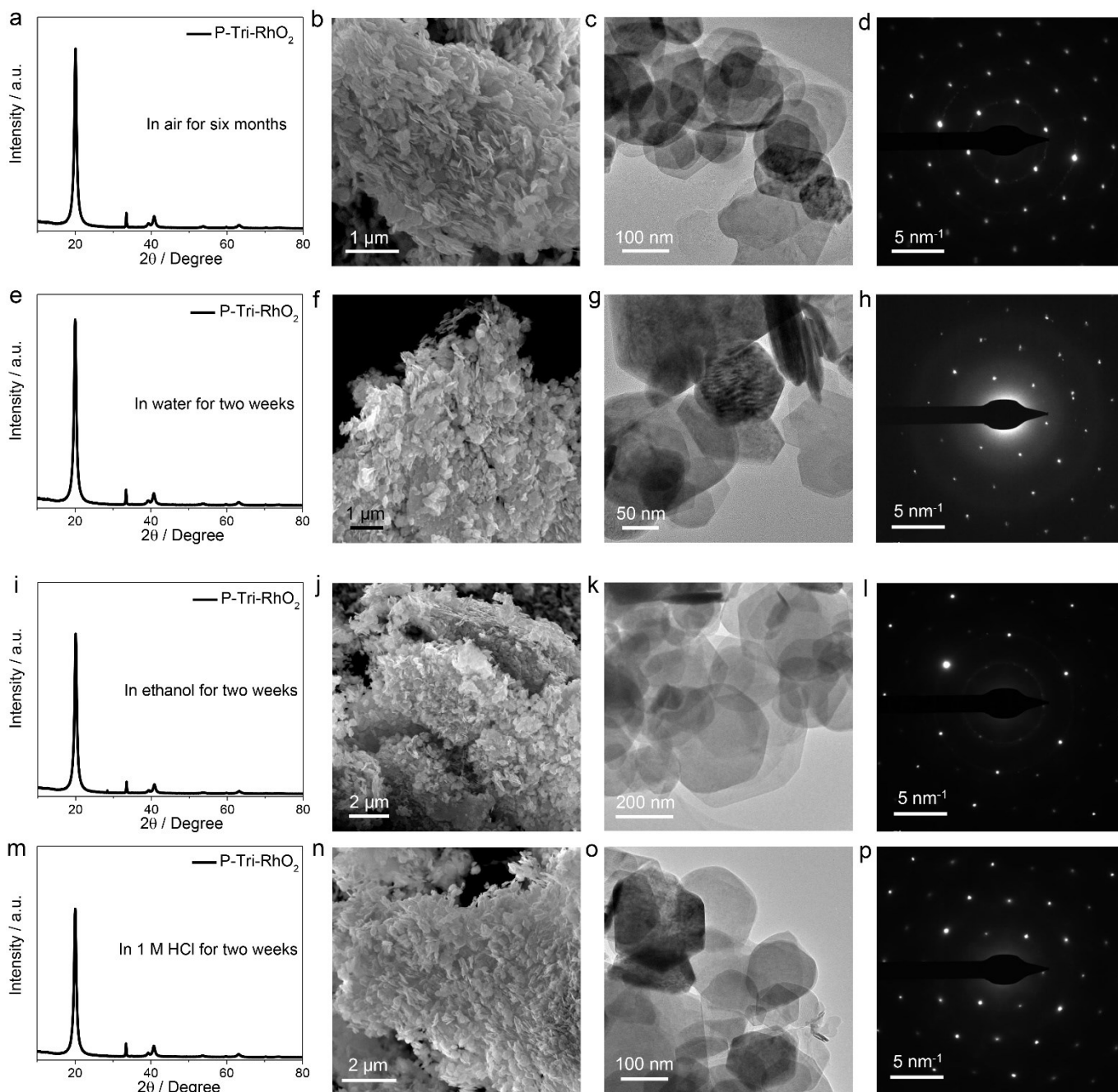
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Supplementary Figure 8. EXAFS fitting curves and wavelet transforms for P-Tri-RhO₂, Rh-NA/RhO₂ and Rh foil. (a), (d), (g) EXAFS fitting curves of P-Tri-RhO₂, Rh-NA/RhO₂ and Rh foil at *R* space. (b), (e), (h) EXAFS fitting curves of P-Tri-RhO₂, Rh-NA/RhO₂ and Rh foil at *q* space. (c), (f), (i) Wavelet transforms of Rh K-edge EXAFS for P-Tri-RhO₂, Rh-NA/RhO₂ and Rh foil.

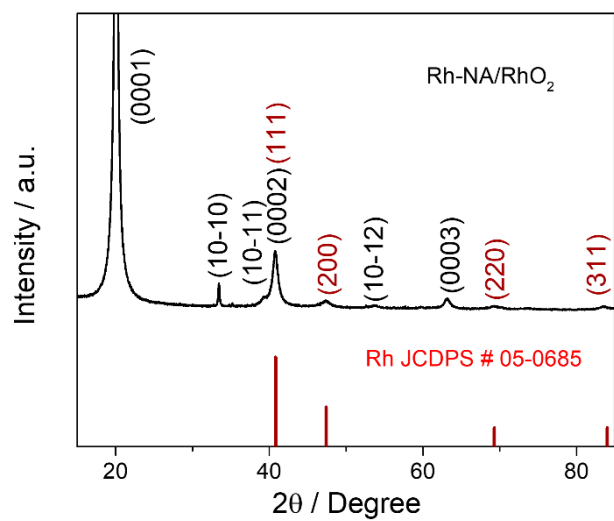


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 2 **Supplementary Figure 9. XRD patterns and SEM images obtained by changing the synthetic**
 3 **parameters. (a) XRD pattern and (b) SEM image of the product obtained by directly mixing RhCl_3 and**
 4 **KOH. (c) XRD pattern and (d) SEM image of the product obtained by directly radio-frequency heating**
 5 **RhCl_3 without adding KOH.**



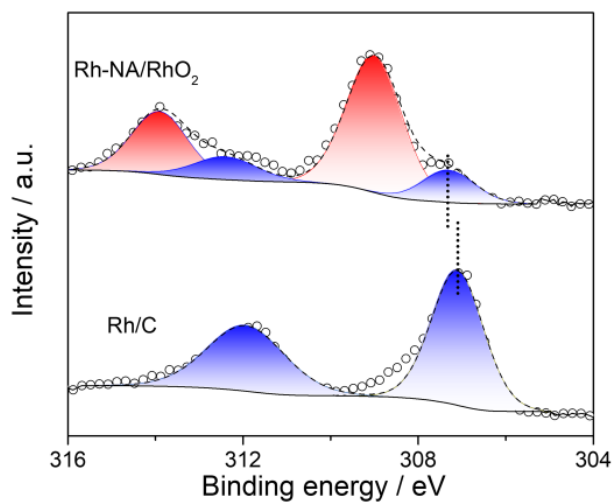
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2 **Supplementary Figure 10. The chemical stability for P-Tri-RhO₂.** (a-d) The XRD pattern, SEM, TEM
 3 images and SAED pattern of P-Tri-RhO₂ after placing it in air for six months. (e-h) The XRD pattern,
 4 SEM, TEM images and SAED pattern of P-Tri-RhO₂ after soaking it in water for two weeks. (i-l) The
 5 XRD pattern, SEM, TEM images and SAED pattern of P-Tri-RhO₂ after soaking it in ethanol for two
 6 weeks. (m-p) The XRD pattern, SEM, TEM images and SAED pattern of P-Tri-RhO₂ after soaking it in 1
 7 M hydrochloric acid solution for two weeks.

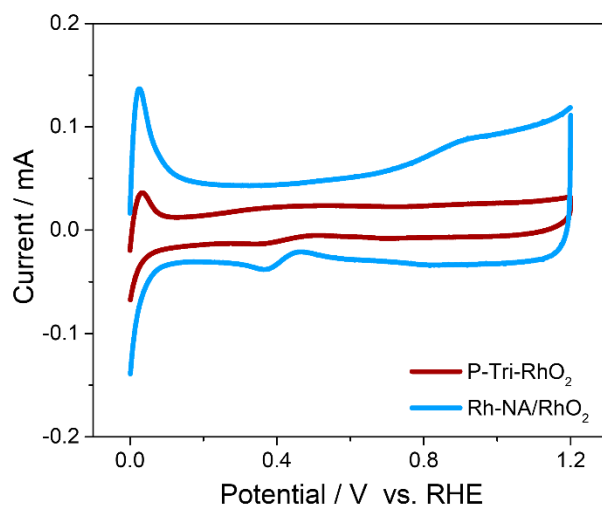


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2 **Supplementary Figure 11. XRD pattern of Rh-NA/RhO₂.** The peaks of (111), (200), (220) and (311)
3 planes of face-centered cubic Rh was detected and marked in red.

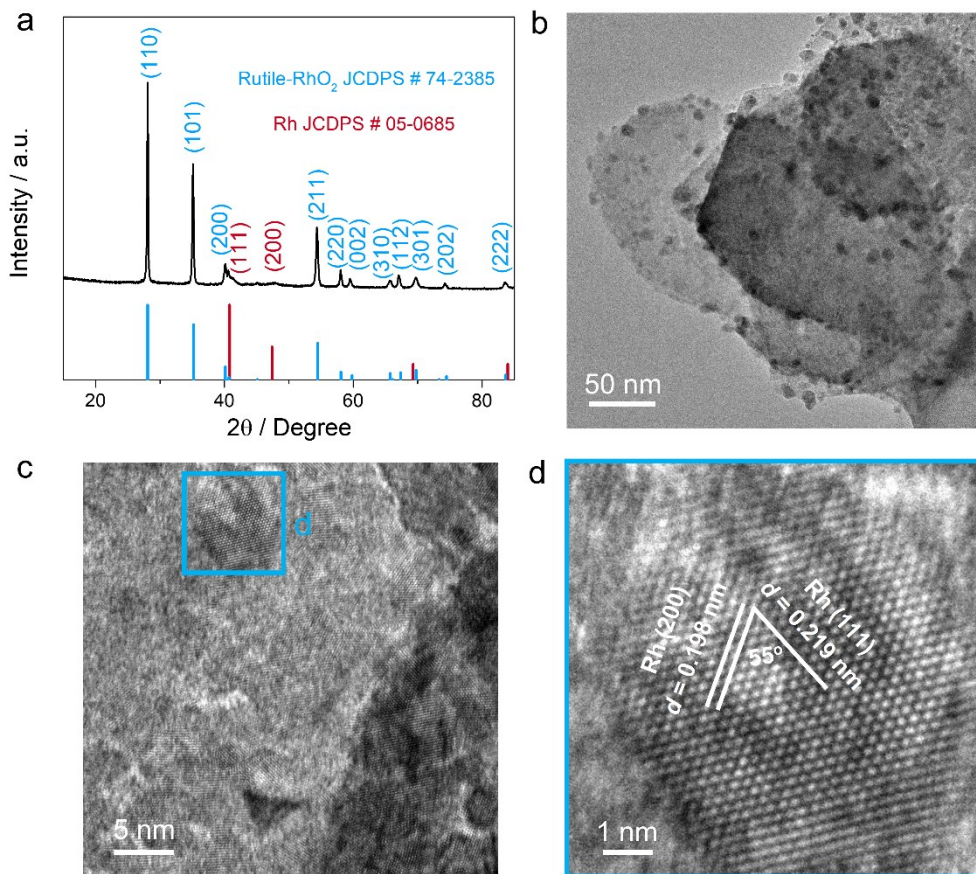


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2 **Supplementary Figure 12. XPS measurements for Rh-NA/RhO₂ and Rh/C. XPS spectra of Rh 3d**
3 **peaks for Rh-NA/RhO₂ and Rh/C.**

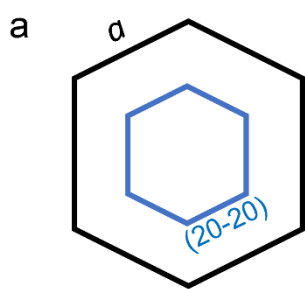


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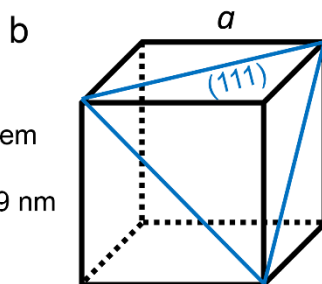
2 **Supplementary Figure 13. Cyclic voltammetry (CV) tests for P-Tri-RhO₂ and Rh-NA/RhO₂. CV**
3 **curves of P-Tri-RhO₂ and Rh-NA/RhO₂ in H₂-saturated 0.5 M H₂SO₄.**



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 2 **Supplementary Figure 14. XRD pattern, TEM and HRTEM images of the product obtained by**
 3 ***in-situ* electroreduction of Rutile-RhO₂.** (a) XRD pattern of the product obtained by *in-situ*
 4 electroreduction of Rutile-RhO₂. (b-d) TEM and HRTEM images of the product obtained by *in-situ*
 5 electroreduction of Rutile-RhO₂.



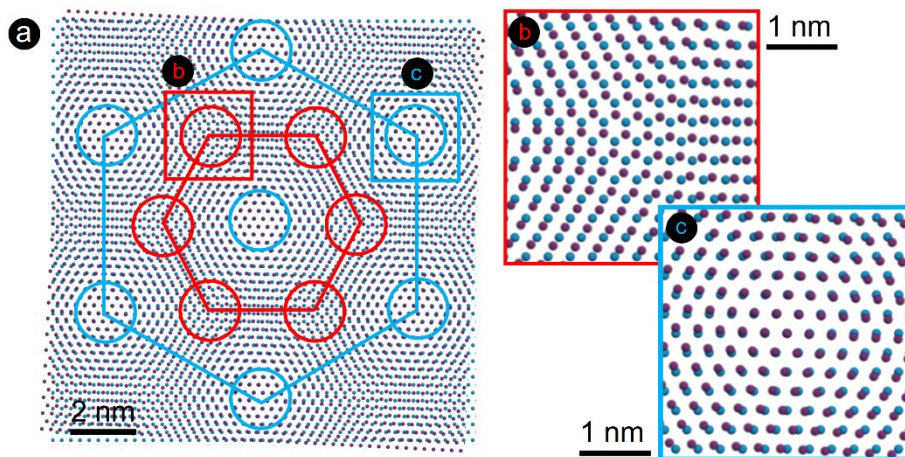
P-Tri-RhO₂ : Trigonal system
 $a = 0.3091 \text{ nm}$
 $d\text{-spacing (20-20)} : 0.1339 \text{ nm}$



Rh : Cubic system
 $a = 0.3803 \text{ nm}$
 $d\text{-spacing (220)} : 0.1345 \text{ nm}$

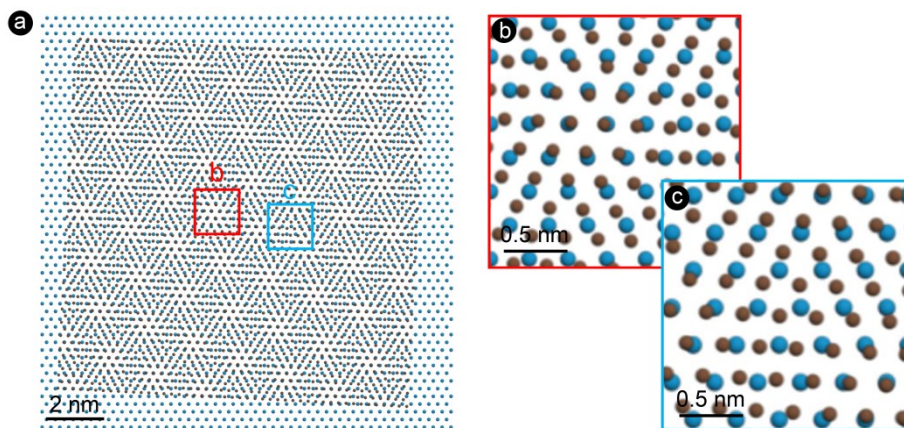
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2 **Supplementary Figure 15. Schematic views of crystal matching of Rh-NA/RhO₂ system. (a)** The
 3 crystal structure information of P-Tri-RhO₂. **(b)** The crystal structure information of face-centered cubic
 4 Rh.



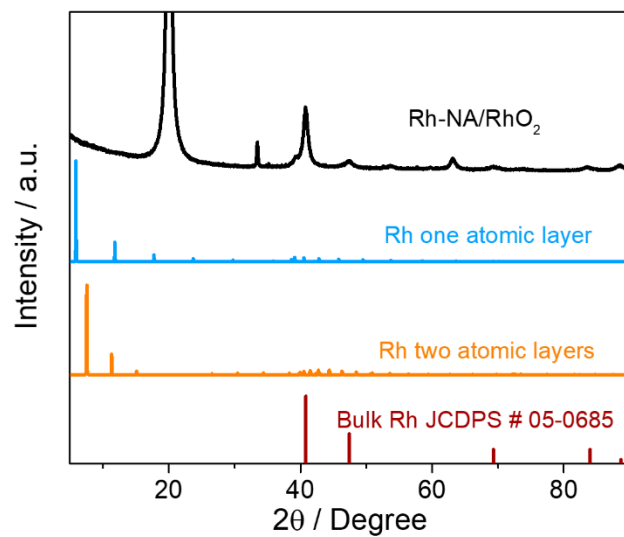
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Supplementary Figure 16. Schematic views of Moire pattern obtained by twisting bilayer P-Tri-RhO₂ region with the rotation angle of 3°. (a) Simulated Moire pattern was obtained by twisting bilayer P-Tri-RhO₂ region with the rotation angle of 3°. The Rh atoms on different layers are marked with red and blue colors, respectively. (b, c) The enlarged areas from (a).

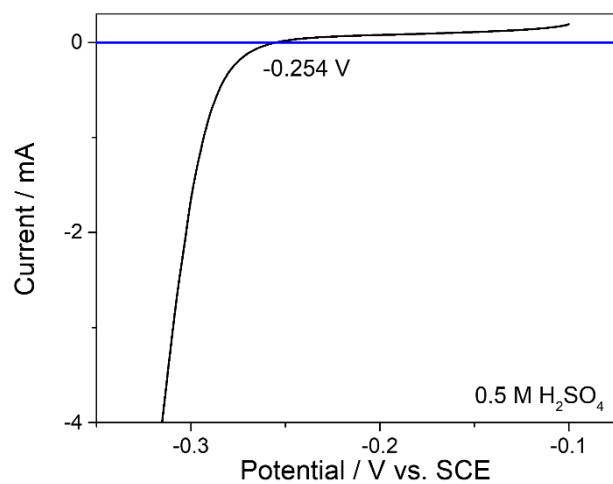


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Supplementary Figure 17. Schematic views of Moire pattern obtained by twisting one single-layer P-Tri-RhO₂ and one single-layer metallic Rh with the rotation angle of 3°. Simulated Moire pattern was obtained by twisting one single-layer P-Tri-RhO₂ and one single-layer metallic Rh with the rotation angle of 3°. (b, c) The enlarged areas from (a).

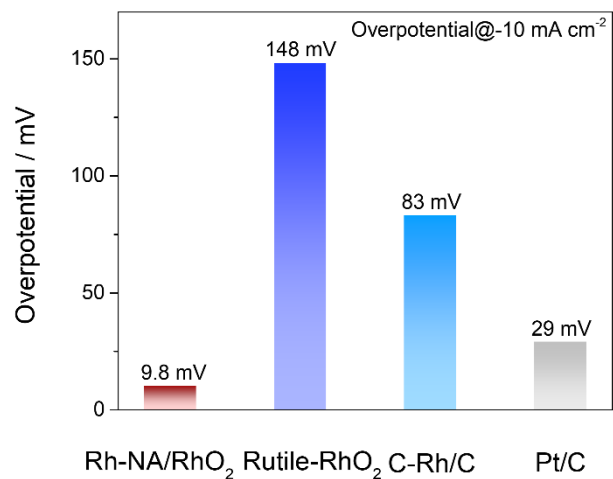


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2 **Supplementary Figure 18. Comparison of XRD patterns for Rh-NA/RhO₂ and different layers Rh.**
3 The XRD pattern of Rh-NA/RhO₂ and the simulated XRD patterns of different layers Rh.



1

2 **Supplementary Figure 19. Calibration of the saturated calomel electrode (SCE).** Calibration of the
3 SCE electrode with respect to reversible hydrogen electrode (RHE) in 0.5 M H₂SO₄ electrolyte bubbled
4 with pure hydrogen gas at room temperature. Scan rate: 5 mV s⁻¹. Two Pt electrodes were used as the
5 working and counter electrodes to calibrate the SCE.



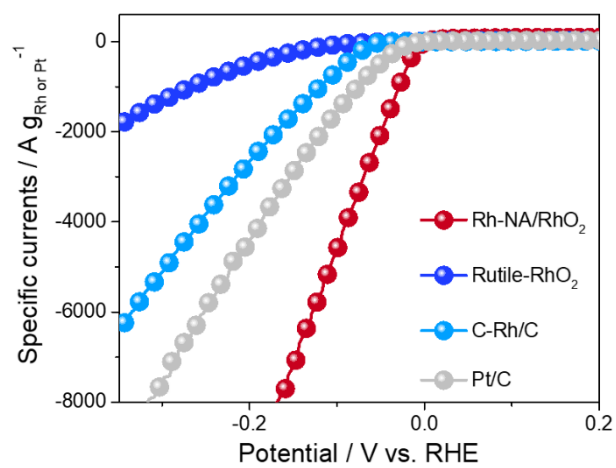
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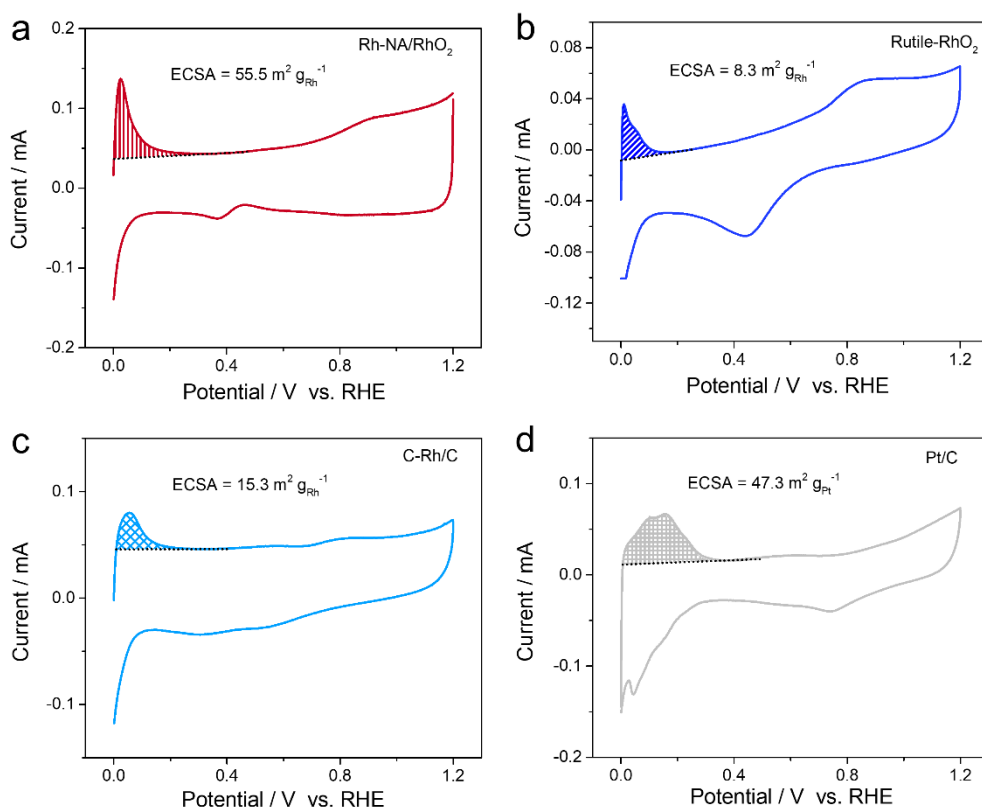
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Supplementary Figure 20. Comparison of overpotentials for different catalysts. The overpotentials at the current density of -10 mA cm^{-2} for Rh-NA/RhO₂, Rutile-RhO₂, C-Rh/C and Pt/C.



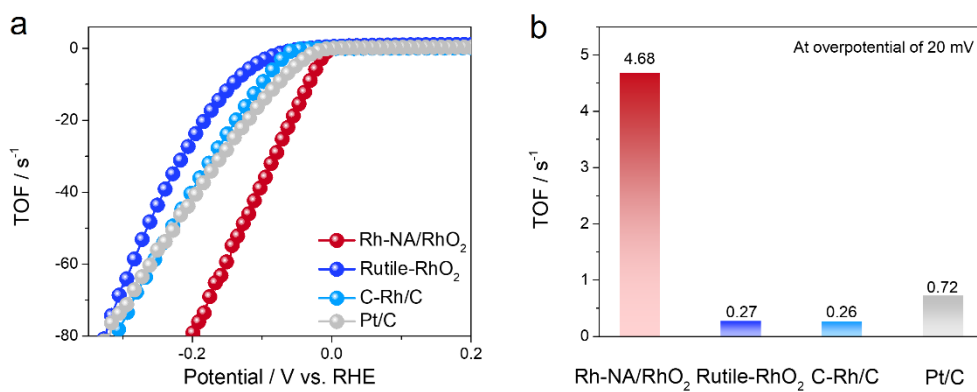
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2 **Supplementary Figure 21. The comparison of specific currents for different catalysts.** The specific
3 currents of Rh-NA/RhO₂, Rutile-RhO₂, C-Rh/C and Pt/C in 0.5 M H₂SO₄.



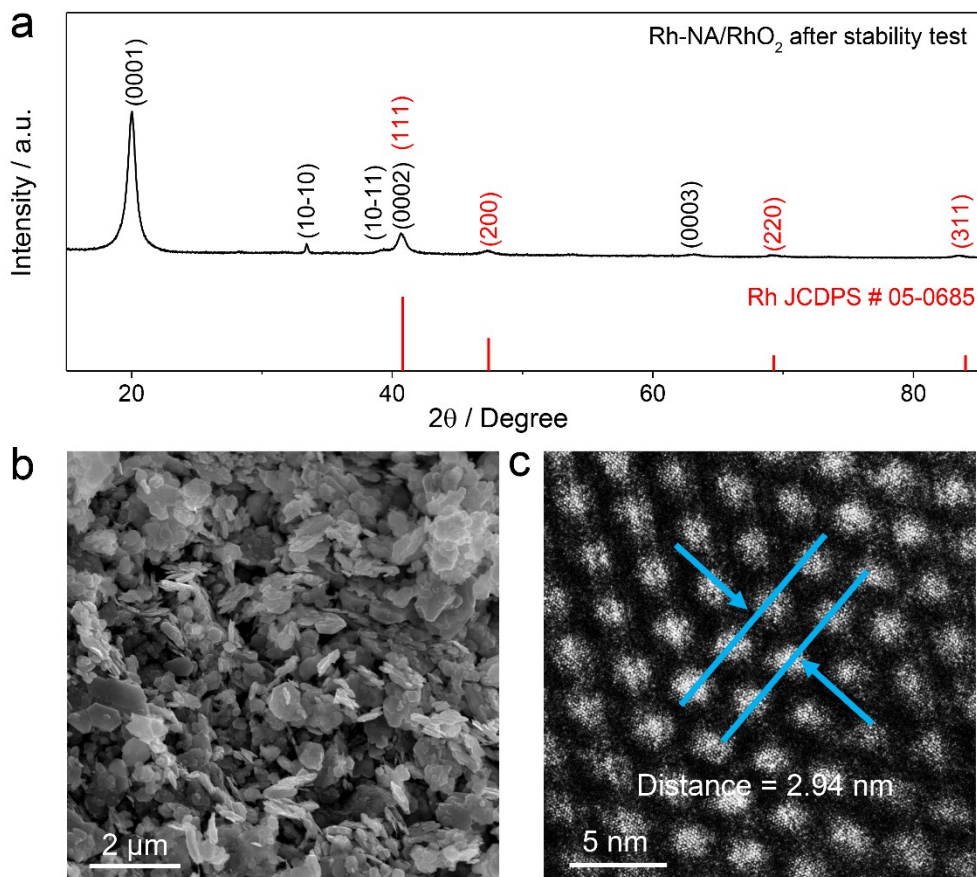
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Supplementary Figure 22. The calculations of ECSA for different catalysts. CV curves of (a) Rh-NA/RhO₂, (b) Rutile-RhO₂, (c) C-Rh/C and (d) Pt/C in H₂-saturated 0.5 M H₂SO₄ with a scan rate of 50 mV s⁻¹.

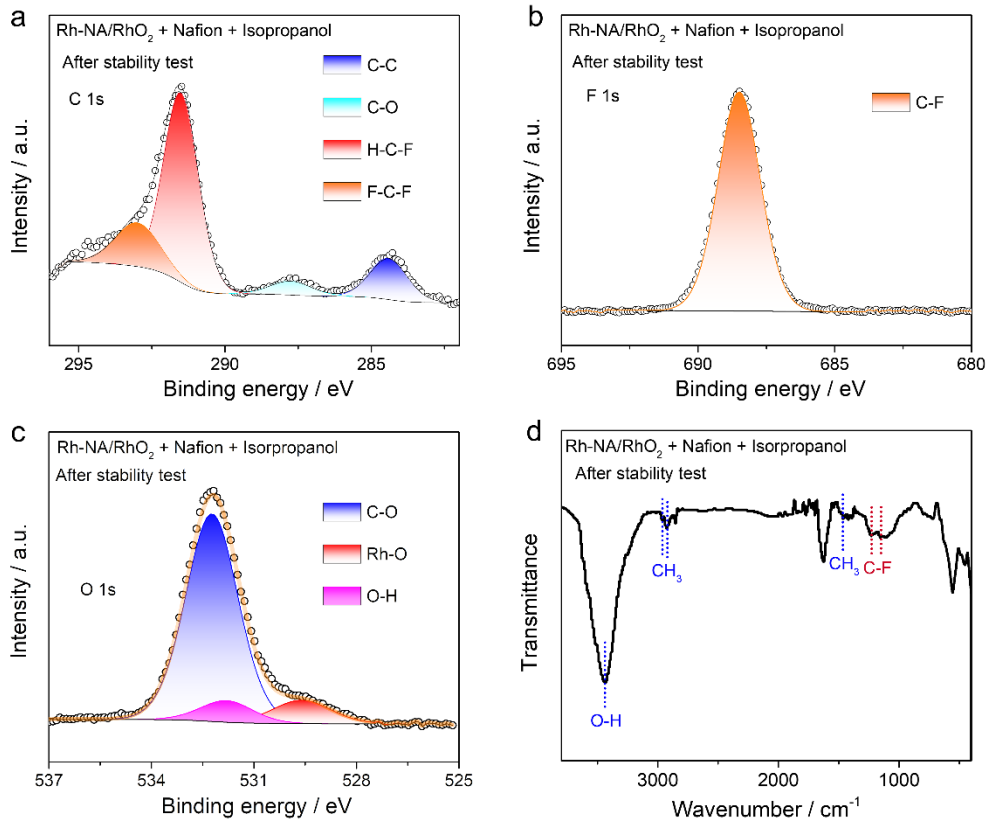


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2 **Supplementary Figure 23. The calculations of TOFs for different catalysts. (a)** The comparison of
 3 TOFs for Rh-NA/RhO₂, Rutile-RhO₂, C-Rh/C and Pt/C at different potentials (vs. RHE). **(b)** The TOFs of
 4 Rh-NA/RhO₂, Rutile-RhO₂, C-Rh/C and Pt/C at the overpotential of 0.1 V.



1
 2 **Supplementary Figure 24. XRD pattern, SEM and STEM images of Rh-NA/RhO₂ after stability test.**
 3 (a) The XRD pattern of Rh-NA/RhO₂ after long-term HER stability test, where the (111), (200), (220) and
 4 (311) planes of face-centered cubic Rh was detected and marked in red. (b, c) SEM and STEM images of
 5 Rh-NA/RhO₂ after long-term HER stability test.



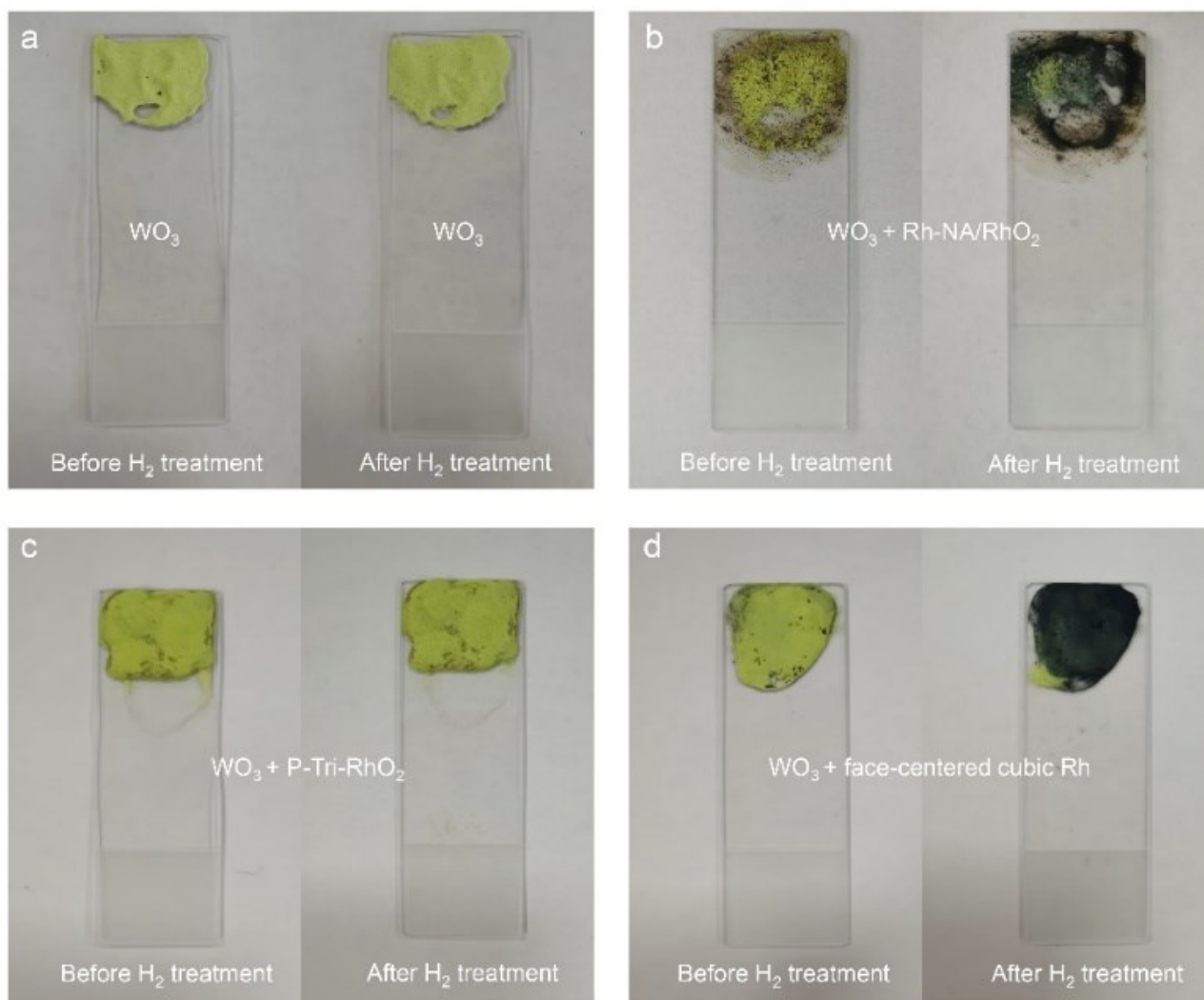
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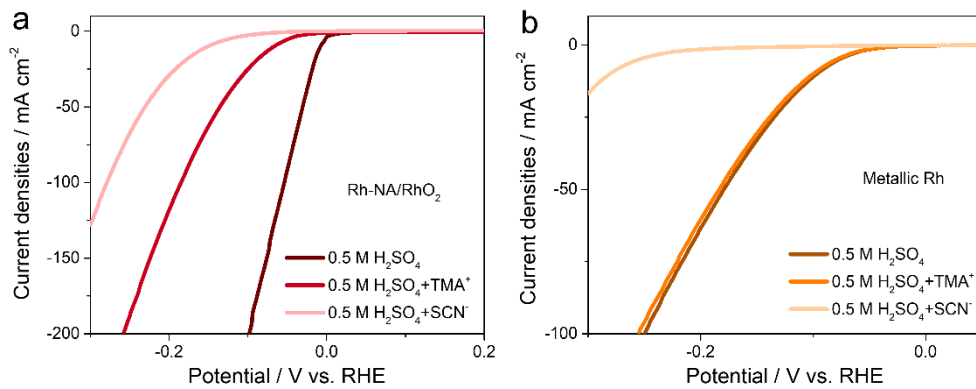
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Supplementary Figure 25. XPS and FTIR measurements of Rh-NA/RhO₂ after long-term HER stability test. XPS spectra of (a) C 1s, (b) F 1s and (c) O 1s for Rh-NA/RhO₂ after long-term HER stability test. (d) FTIR spectrum of Rh-NA/RhO₂ after long-term HER stability test.

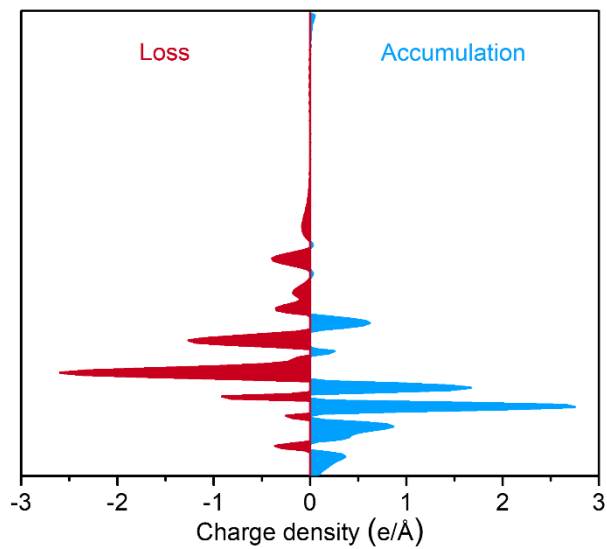


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2 **Supplementary Figure 26. The measurements of hydrogen spillover for Rh-NA/RhO₂.** (a) The
 3 photographic image of WO₃ before and after H₂ treatment at room temperature. clearly showing no color
 4 change after H₂ treatment. (b) The photographic image of physical mixture for Rh-NA/RhO₂ and WO₃
 5 before and after H₂ treatment at room temperature, clearly showing the color change of WO₃ from yellow
 6 to dark blue after H₂ treatment. (c) The photographic image of physical mixture P-Tri-RhO₂ and WO₃
 7 before and after H₂ treatment at room temperature, clearly showing no color change after H₂ treatment. (d)
 8 The photographic image of physical mixture Rh and WO₃ before and after H₂ treatment at room
 9 temperature, clearly showing the color change of WO₃ from yellow to dark blue after H₂ treatment.



1
 2 **Supplementary Figure 27. Poison experiment for Rh-NA/RhO₂.** Polarization curves for (a)
 3 Rh-NA/RhO₂ and (b) Rh before and after the addition of SCN⁻ or TMA⁺ ions in 0.5 M H₂SO₄.



1
2 **Supplementary Figure 28. Charge density difference of Rh-NA/RhO₂.** Charge density difference of
3 Rh-NA/RhO₂ along z direction.

1 **Supplementary Tables**2 **Supplementary Table 1. Crystallographic information for P-Tri-RhO₂ and Rutile-RhO₂.**

Material	Crystal system	Bravais lattice	Unit-cell dimensions	Space group
			$a = b = 3.091 \pm 0.004 \text{ \AA}, c =$	
P-Tri-RhO₂	Trigonal	Primitive	$4.407 \pm 0.004 \text{ \AA};$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	P-3m1 (164)
			$a = b = 4.489 \text{ \AA},$	
Rutile-RhO₂	Tetragonal	Primitive	$c = 3.090 \text{ \AA};$ $\alpha = \beta = \gamma = 90^\circ$	P4₂/mnm (136)

3

1 **Supplementary Table 2. The hydrogen underpotential deposition-based area and BET values of**
2 **P-Tri-RhO₂, Rh-NA/RhO₂, Rutile-RhO₂, C-Rh/C and Pt/C.**

Catalyst	Hydrogen under potential deposition-based area / m² g⁻¹	BET area / m² g⁻¹
P-Tri-RhO₂	8.8 ± 0.12	30.3 ± 0.82
Rh-NA/RhO₂	55.5 ± 1.13	/
Rutile-RhO₂	8.3 ± 0.2	9.5 ± 0.25
C-Rh/C	15.3 ± 0.31	147.1 ± 3.01
Pt/C	47.3 ± 1.01	137.9 ± 2.82

3

1 **Supplementary Table 3. The SDs of Rh atoms for different Moire patterns and Rh-NA/RhO₂.**

Structure	The theoretical range of SD for different Moire patterns / nm⁻²	The SDs for Rh-NA/RhO₂ / nm⁻²
Rh-NA/RhO₂	/	47.904 (theoretical) / 47.3±1.2 (actual)
Moire pattern with two layer of P-Tri-RhO ₂	12.086~24.172	/
Moire pattern with two layer of metallic Rh	15.969~31.938	/
Moire pattern with one layer of P-Tri-RhO ₂ and one layer of metallic Rh	12.086~28.055	/

2

1 **Supplementary Table 4. The HER activities of Rh-NA/RhO₂, Rutile-RhO₂, C-Rh/C and Pt/C in 0.5**
 2 **M H₂SO₄*.**

Catalyst	Overpotential @ 10 mA cm⁻² / mV	Geometric activity / mA cm⁻²	Mass activity / mA mg_{Rh or Pt}⁻¹	Tafel slope / mV dec⁻¹
Rh-NA/RhO₂	9.8 ± 0.61	200 ± 4.0	4634 ± 30.0	24.0
Rutile-RhO₂	148 ± 2.4	3 ± 0.1	67 ± 0.9	99.1
C-Rh/C	83 ± 1.6	17 ± 0.2	601 ± 5.2	43.7
Pt/C	29 ± 0.9	85 ± 1.8	1502 ± 12.8	30.0

3 *The geometric activity and mass activity were obtained at -0.1 V vs. RHE.

1 **Supplementary Table 5. The exchange current density (j_0) of Rh-NA/RhO₂, Rutile-RhO₂, C-Rh/C**
2 **and Pt/C in 0.5 M H₂SO₄.**

Catalysts	Exchange current density / mA cm⁻²
Rh-NA/RhO₂	-3.356 ± 0.1258
Rutile-RhO₂	-0.561 ± 0.0015
C-Rh/C	-0.142 ± 0.0003
Pt/C	-1.220 ± 0.0430

3

1 **Supplementary Table 6. The comparison of HER activity performances of Rh-NA/RhO₂ with**
 2 **previous reported electrocatalysts.**

Catalyst	Substrate	Electrolyte	Overpotential @ 10 mA cm ⁻² / mV	Tafel slope / mV dec ⁻¹	Supplementary References
Rh-NA/RhO₂	GCE	0.5 M H₂SO₄	9.8	24.0	This work
PdCoO₂	GCE	1 M H ₂ SO ₄	15	38	1
Pt₁/OLC	GCE	0.5 M H ₂ SO ₄	38	36	2
Pt-GT-1	GCE	0.1 M HClO ₄	18	24	3
Pd₃P₂S₈	GCE	0.5 M H ₂ SO ₄	91	29	4
Ru@C₂N	GCE	0.5 M H ₂ SO ₄	13.5	30	5
Pt-SAs/TMDs	GCE	0.5 M H ₂ SO ₄	32	28	6
RuIr-NC	RDE	0.5 M H ₂ SO ₄	46	32	7
1%Pd-MoS₂/CP	GCE	0.5 M H ₂ SO ₄	78	32	8
Rh₂P	GCE	0.5 M H ₂ SO ₄	14	31.7	9
Rh NS/C	GCE	0.1 M HClO ₄	15.8	61.5	10
Au-Rh	RDE	0.5 M H ₂ SO ₄	20	29	11
Rh-MoS₂	RDE	0.5 M H ₂ SO ₄	67	54	12
Rh₂S₃- ThickHNP/C	GCE	0.5 M H ₂ SO ₄	88	44	13
a-RuTe₂ PNRs	GCE	0.5 M H ₂ SO ₄	33	35	14
RuCu NPs	GCE	0.5 M H ₂ SO ₄	19	26	15
Pt-PVP/TNR@GC	RDE	0.5 M H ₂ SO ₄	21	27	16
PdCu/Ir	GCE	0.1 M HClO ₄	20	59.6	17

RuIrO_x	RDE	0.5 M H ₂ SO ₄	12	23	18
Pt₅/HMCS	RDE	0.5 M H ₂ SO ₄	20.7	28.3	19
AL-Pt/Pd₃Pb	GCE	0.5 M H ₂ SO ₄	13.8	18	20
Pt-AC/DG	GCE	0.1 M HClO ₄	21	27.5	21

1

1 **Supplementary Table 7. The comparison of minimum cluster size and minimum interparticle**
 2 **distance with previous reported materials.**

Materials	Minimum cluster size	Minimum inter-particle distance	Minimum inter-surface distance	Preparation method	Supplementary References
Rh-NA/RhO₂	3.2 nm	3.709 nm	0.5 nm	In situ formed Rh nanoarrays on metastable trigonal phase RhO₂ nanosheets	This work
As₂Se₃-PVDF core-shell	~200 nm	~800 nm	~1 μm	Melting commercially bought glasses	22
Fe₃O₄ NCA	~8 nm	~10.7 nm	~3 nm	Controlled thermal decomposition	23
SHNO arrays	50 nm	100 nm	~115 nm	Ultra-high vacuum magnetron sputtering machine	24
3D gold nanostructures	5.8 nm	7.1 nm	~3 nm	Pressure-directed assembly (PDA)	25
Platinum nanoparticle array	40 nm	150 nm	~100 nm	Electron beam lithography (EBL)	26
Au@Ag core-shell	17 nm	45 nm	~30 nm	Block copolymer (BCP) lithography	27
Nanopattern apertures	12 nm	100 nm	33 nm	Focused-ion-beam-guided pre patterning technique	28
AgNC array	100 nm	2000 nm	1.8 μm	Directed assembly of silver nanocubes (AgNCs) onto TiO ₂ coated Si substrates.	29
Ag nanoparticle arrays	200 nm	540 nm	~296 nm	Thermal evaporation and focused-ion beam	30
Pt nanoparticle (NP) arrays	/	57 nm	~25 nm	Electrochemical anodization process	31
Au_{0.5}Pt_{0.5} alloy	6 nm	20 nm	~26 nm	Block copolymer micellar nanoLithography (BCML)	32
Si₃N₄	15 nm	100 nm	~73.5 nm	EUV interference lithography	33
Platinum	28 nm	100 nm	~100 nm	Electron beam	34

nanoparticle array	lithography (EBL)				
Cu NPs arrays	110 nm	350 nm	~206 nm	Interfacial self-assembly	35
Fe₂O₃ nanoparticle array	9.01 nm	19.23 nm	~16.3 nm	Block copolymer lithography	36
Au nanoparticle arrays	2.4 nm	26.8 nm	~24.4 nm	Ar plasma treatment	37
Pt nanoparticle arrays	2.2 nm	10.8 nm	~23.4 nm	PS-b-P2VP diblock-copolymers	38
Si_{0.5}CeO_{0.5}	5 nm	10 nm	~7 nm	Co-self-assembling route	39
Au nanoparticles	5.8 nm	10.5 nm	~2.1 nm	Asymmetric heating of a novel precursor	40
Pt Nanoparticle Arrays	20 nm	150 nm	~135 nm	Electron beam lithography (EBL)	41
Pt nanoparticle arrays	28 nm	100 nm	~162 nm	Electron beam lithography (EBL)	42
Platinum cluster arrays	50 nm	200 nm	~73.7 nm	Electron beam lithography (EBL)	43

1

1 Supplementary Notes

2 Supplementary Note 1. The calculation of surface densities (SDs) of Rh atoms for different Moire 3 patterns and Rh-NA/RhO₂.

4 1. For Moire patterns consisting of two single-layer P-Tri-RhO₂

5 For a single-layer P-Tri-RhO₂, the surface density of Rh atom is:

$$SD = 1 \div \left(\frac{\sqrt{3}}{2} \times 0.3091^2 \text{ nm}^2 \right) = 12.086 \text{ nm}^{-2}$$

6 If Moire patterns were obtained by twisting two single-layer P-Tri-RhO₂ with different rotation angles, the
7 maximum surface density was determined to be $\leq 2 \times 12.086 = 24.172 \text{ nm}^{-2}$. So the range of surface
8 density for Moire patterns obtained by twisting bilayer P-Tri-RhO₂ was determined to be $12.086 \text{ nm}^{-2} \leq$
9 $SD \leq 24.172 \text{ nm}^{-2}$.

10 2. For Moire patterns consisting of two single-layer metallic Rh

11 For a single-layer metallic Rh, the surface density of Rh atom is:

$$SD = 1 \div \left(\frac{\sqrt{3}}{2} \times 0.2689^2 \text{ nm}^2 \right) = 15.969 \text{ nm}^{-2}$$

12 If Moire patterns were obtained by twisting two single-layer metallic Rh with different rotation angles, the
13 maximum surface density was determined to be $2 \times 15.969 = 31.938 \text{ nm}^{-2}$. So the range of surface
14 density for Moire patterns obtained by twisting bilayer face-centered cubic Rh was determined to be
15 $15.969 \text{ nm}^{-2} \leq SD \leq 31.938 \text{ nm}^{-2}$.

16 3. For Moire patterns consisting of one single-layer P-Tri-RhO₂ and one single-layer metallic Rh

17 If Moire patterns were obtained by twisting one single layer P-Tri-RhO₂ and one single layer metallic Rh
18 with different rotation angles, the maximum surface density was determined to be $15.969 + 12.086 =$
19 28.055 nm^{-2} . So the range of surface density for Moire patterns obtained by twisting P-Tri-RhO₂ and
20 metallic Rh was determined to be $12.086 \text{ nm}^{-2} \leq SD \leq 28.055 \text{ nm}^{-2}$.

21 4. For face-centered cubic Rh nanocrystal arrays

22 The theoretical surface density of rhodium atoms for face-centered cubic Rh along the [111] growth
23 direction.

$$SD = 3 \div \left(\frac{\sqrt{3}}{2} \times 0.2689^2 \text{ nm}^2 \right) = 47.904 \text{ nm}^{-2}$$

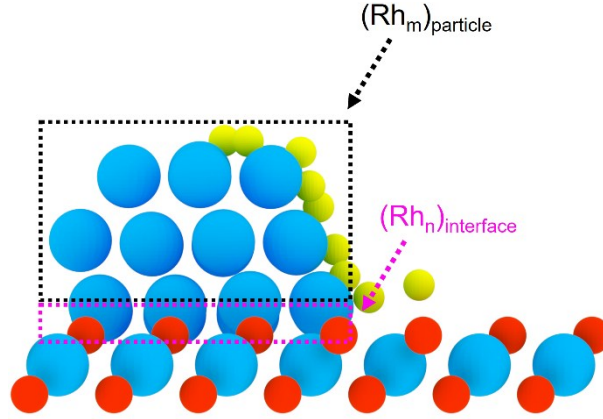
24 5. The actual SD of Rh atoms in Rh-NA/RhO₂ counted from the (scanning transmission electron 25 microscopy) STEM image (Fig. 2f)

26 As shown in Fig. 2f, the actual SD of Rh atoms in Rh-NA/RhO₂ is counted to be $47.3 \pm 1.2 \text{ nm}^{-2}$.

27

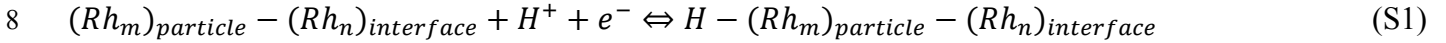
1 **Supplementary Note 2. Proposed H spillover assisted HER mechanism for Rh-NA/RhO₂.**

2 Based on the simulation, a possible path is proposed to explain the electrocatalysis of Rh-NA/RhO₂. HER
3 may take place on any Rh nanoparticles by themselves and with the help of H spillover from Rh
4 nanoparticle to contact interface between Rh nanoparticle and P-Tri-RhO₂ substrate.

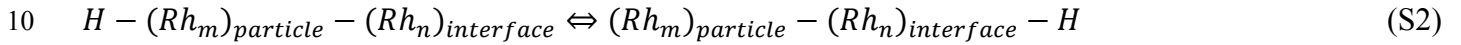


5
6 Assuming that H spillover is from Rh nanoparticle $(Rh_m)_{particle}$ to contact interface $(Rh_n)_{interface}$,

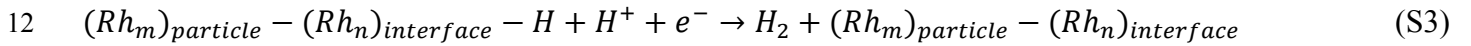
7 the first step is the adsorption of H atom on the surface of Rh nanoparticle $(Rh_m)_{particle}$,



9 Secondly, the spillover of H atom from $(Rh_m)_{particle}$ to $(Rh_n)_{interface}$,



11 Thirdly, the Heyrovsky process on the interface of Rh nanoparticle and P-Tri-RhO₂ $(Rh_n)_{interface}$,



13 The kinetics may be complicated. The reaction velocity of hydrogen evolution may be written as

14 $r = k_3 \theta_{(Rh_n)_{interface}-H} C_{H^+}$, where r is the reaction rate; k the rate constant; θ the fractional
15 occupancy of the H-adsorption sites; and C_{H^+} the concentration of hydrogen ion.

16 In the steady state, for $\theta_{(Rh_n)_{interface}-H}$,

17
$$\frac{d\theta_{(Rh_n)_{interface}-H}}{dt} =$$

18
$$k_2 \theta_{(Rh_m)_{particle}-H} (1 - \theta_{(Rh_n)_{interface}-H}) - k_{-2} \theta_{(Rh_n)_{interface}-H} (1 - \theta_{(Rh_m)_{particle}-H}) -$$

19
$$k_3 \theta_{(Rh_n)_{interface}-H} C_{H^+};$$

20 and for $\theta_{(Rh_m)_{particle}-H}$

$$\begin{aligned}
1 \quad & \frac{d\theta_{(Rh_m)particle-H}}{dt} = k_1(1 - \theta_{(Rh_m)particle-H})C_{H^+} - k_{-1}\theta_{(Rh_m)particle-H} - k_2\theta_{(Rh_m)particle-H}(1 - \\
2 \quad & \theta_{(Rh_n)interface-H}) + k_{-2}\theta_{(Rh_n)interface-H}(1 - \theta_{(Rh_m)particle-H}).
\end{aligned}$$

3 At low overpotential,

$$\begin{aligned}
\theta_{(Rh_n)interface-H} &\approx \frac{k_2\theta_{(Rh_m)particle-H}}{k_2\theta_{(Rh_m)particle-H} + k_{-2} - k_{-2}\theta_{(Rh_m)particle-H} + k_3C_{H^+}} \\
&\approx \frac{k_{20}}{k_{-20}}\theta_{(Rh_m)particle-H}e^{-\frac{F\Delta\phi}{RT}} \\
\theta_{(Rh_m)particle-H} &\approx \frac{k_1C_{H^+} + k_{-2}\theta_{(Rh_n)interface-H}}{k_1C_{H^+} + k_{-1} + k_2 + k_{-2}\theta_{(Rh_n)interface-H} - k_2\theta_{(Rh_n)interface-H}} \approx \frac{k_{10}}{k_{-10}}C_{H^+}e^{-\frac{F\Delta\phi}{RT}}
\end{aligned}$$

$$4 \quad \text{Then, } r = k_3\theta_{(Rh_n)interface-H}C_{H^+} = \frac{k_{10}k_{20}k_{30}}{k_{-10}k_{-20}}C_{H^+}^2e^{-\frac{(2+\alpha)F\Delta\phi}{RT}} \quad (S4)$$

$$5 \quad \text{And } -j = Fr = \frac{k_{10}k_{20}k_{30}}{k_{-10}k_{-20}}FC_{H^+}^2e^{-\frac{(2+\alpha)F\Delta\phi}{RT}}$$

$$6 \quad \lg(-j) = Const + 2 \lg C_{H^+} - \frac{(2+\alpha)F}{2.303RT} \Delta\phi \quad (S5)$$

7 Therefore, the Tafel slope is: $\frac{2.303RT}{(2+\alpha)F} = 0.024 \text{ V dec}^{-1}$ (assuming $\alpha = 0.5$).

8

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