Supporting Information for

Stabilizing Rh Nanoparticles by TiO₂ Array with Oxygen Vacancies for High-performance pH-wide Hydrogen Evolution

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Characterization. To acquire the X-ray diffraction (XRD) data, a X'Pert3 Powder diffractometer from PANalytical B.V. (Netherlands) was utilized, equipped with Cu K α radiation ($\lambda = 0.15405$ nm), operated at 40 kV and 40 mA, respectively. For scanning electron microscopy (SEM), a Zeiss Sigma 500 (Germany) was employed. Additionally, the acquisition of transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images was facilitated by the JEM-2100F instrument from JEOL (Japan). X-ray photo-electron spectra (XPS) was performed on Thermo Scientific K-Alpha+ (Thermo Fisher, Waltham, America) using Mono Al Ka X-ray radiation.

Theoretical calculations. For theoretical calculations, the Vienna Ab Initio Package (VASP) was used to perform density functional theory (DFT) calculations within the generalized gradient approximation (GGA) framework, specifically the Perdew-Burke-Ernzerhof (PBE) formulation.^[1-3] Ionic cores were modeled using projected augmented wave (PAW) potentials, with a plane wave basis set cutoff of 450 eV.^[4,5] Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method with a width of 0.05 eV. Gaussian smearing (width = 0.05 eV) was applied to allow partial occupancies of Kohn-Sham orbitals. Self-consistency was achieved with an energy change threshold of 10^{-5} eV. Geometry optimization was considered convergent when force changes fell below 0.05 eV/Å. Grimme's DFT-D3 methodology was employed to account for the dispersion interactions, with a vacuum spacing of 20 Å perpendicular to the structure's plane.^[6] The Brillouin zone integral utilized the surfaces structures of $1 \times 1 \times 1$ Monkhorst-Pack K-point sampling. Adsorption energies(Eads) were calculated as Eads= Ead/sub -Ead -Esub, where Ead/sub, Ead, and Esub are the total energies of the optimized adsorbate/substrate system, the adsorbate in the structure, and the clean substrate, respectively. The density of states had been investigated using $2 \times 2 \times 1$ Monkhorst-Pack scheme k-point mesh for structures adsorbed. The free energy was calculated using the equation:

G=Eads+ZPE-TS

where G, Eads, ZPE and TS are the free energy, total energy from DFT calculations, zero point energy and entropic contributions, respectively.

To investigate disorder structures, Ab initio molecular dynamics (AIMD) simulation was conducted with a cut-off energy of 450 eV for optimizations. The Brillouin zone was sampled by a

Monkhorst-Pack (MP) k-point grid of $1 \times 1 \times 1$ for geometry optimizations. The PBE-D3 dispersion term was introduced to correct the van der Waals interactions. The conjugated gradient method was applied with a smearing width of 0.1 eV, and the convergence criteria for the energy and force were 10^{-5} eV/cell and 0.05 eV/Å, respectively. AIMD simulations were run for 10 ps as equilibration with time steps of 1 fs, performing a constant temperature of 400 K in the Nosé-Hoover isokinetic ensemble.

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Figure S1 (a-d) SEM images and element mapping, (e) corresponding EDX image of $Rh/TiO_2/Ti$ (inset is the mass ratio of elements). (f) Photograph of TiO_2 nanoarrays prepared with pure EG.



Figure S2 SEM images and photographs of TiO_2 nanoarrays prepared with (a-c) pure H₂O, and mixed solutions of H₂O and EG at volume ratios of (d-f) 4:1, (g-i) 1:1, and (j-l) 1:4, respectively.



Figure S3 SEM images of (a-c) TiO_2 and (d-f) Rh/ TiO_2 *in-situ* grown onto Ti sheet. (g-i) SEM images of Rh nanoparticles deposited onto Ti foam.



Figure S4 The statistical analysis of Rh particle size.



Figure S5 (a) LSV curves, and (b) mass activity comparison of Rh/TiO₂/Ti with various Rh loadings in 1.0 M KOH. The Rh loadings of Rh/TiO₂/Ti (1), Rh/TiO₂/Ti (2), and Rh/TiO₂/Ti (3) are 28, 35, and 47 μ g/cm², respectively.



Figure S6 Polarization curves of different samples in 1.0 M KOH.



Figure S7 Enlarged Nyquist plots of Rh/TiO₂/Ti, TiO₂/Ti, Rh/Ti and commercial Pt/C in Figure 4d.



Figure S8 CV curves of (a) Rh/TiO₂/Ti, (b) Rh/Ti, and (c) TiO_2/Ti at various scan rates in alkaline

condition.



Figure S9 (a, b) Low-magnification and (b) high-magnification SEM characterizations of Rh/TiO₂/Ti after 10000 CV cycling in 1.0 M KOH. (c-f) Element mapping of Rh, O and Ti for the catalyst Rh/TiO₂/Ti after 10000 CV cycling in 1.0 M KOH.



Figure S10 XRD characterizations of initial Rh/TiO₂/Ti and Rh/TiO₂/Ti after 10000 CV cycling and CP test over 120 hours in 1.0 M KOH.



Figure S11 (a) SEM image and (b-d) element mapping of Rh, O and Ti of Rh/TiO₂/Ti after CP test in 1.0 M KOH over 120 hours.



Figure S12 Enlarged Nyquist plots of Rh/TiO₂/Ti, TiO₂/Ti, Rh/Ti and commercial Pt/C in Figure





Figure S13 CV curves at various scan rates of (a) $Rh/TiO_2/Ti$, (b) Rh/Ti, and (c) TiO_2/Ti in acidic condition.



Figure S14 Hydrophilicity of TiO_2/Ti and $Rh/TiO_2/Ti$. The contact angles of the water droplets on (a) TiO_2/Ti and (b) $Rh/TiO_2/Ti$.

Catalysts	Overpotential / mV (@10 mA cm ⁻²)	Tafel Slope / mV dec ⁻¹	Stability/h	References
Rh ₂ O ₃ - NiWO ₄ /PNF	34	18	100	J. Colloid Interface Sci. 2024, 659, 895-904.
5wt% Rh-WO ₃	116	73	14	Int. J. Hydrog. Energy 2023, 48 (84), 32686- 32698.
Rh-O-W	8	24.6	50	ACS Nano 2023, 17 (11), 10733-10747.
MoOx-Rh/C	15	16	12	Angew. Chem.Int. Ed. 2022, 61 (34), 8.
RhNiP MNs	36	28	20	Chem. Eng. J. 2021,426,8.
Rh(OH) ₃ /CoP	13	24	70	Adv. Energy Mater. 2023, 13 (44), 10.
Rh _x N-NC	16	43	10	Small 2024, 20 (14), 9.
RhPd-H	40	35.7	10	J. Am. Chem. Soc. 2020, 142, 3645
Rh _x P@NPC	69	80	10	Adv. Funct. Mater. 2019, 29,1901790
Rh-Rh ₂ P@C	37	32	32	J. Mater. Chem. A 2020, 8, 12378
Pt/TC	58	65.5	10	ACS Appl. Mater. Interfaces 2024, 16 (20), 26044-26056.
PtSe ₂ /Pt	42	53	48	Angew. Chem., Int. Ed. 2021, 60, 23388

 Table S1 Performance of recently Rh-based catalysts in 1.0M KOH.

PtNi-O/C		39.8		78.8		10		J. Am. Chem. Soc. 2018, 140, 9046
Catalysts PdH _x @Ru	(/ n	Overpotential mV (@10 nA cm ⁻²)	ך /	afel Slope mV dec ⁻¹	Stab /h	oility	Reference 25	Ces J. Am. Chem. Soc. 2023, 145, 5710
⁵ wt% Rh- RuP/NP-C WO ₃		⁴⁸ 54		31 49	1	4	Int. J. Hy 32686-32	/drog. Energy 2023, 48(84), Chem. Eng. J. 2022, 429, 2698 132557
Rh-O-W		7		23	5	0	ACS Nat	no 2023, 17 (11), 10733-
N-RuP/NPC		29.6		35			20 747.	Nano Energy 2020, 77, 105212
Rh-GO		22		10		2	ACS Apj (12) 122	pl. Nano Mater. 2020, 3
MoP-		47		36.9			12), 122	Appl. Catal. B Environ.
mProPANS		47		32	1	2	Small 20	24,020,(343, 9.20879
RuCo/MQ3GnDs 900	_	6026		4261.65	2	4	2 9ont. Er	neASS2624,ai8a(b); Sb91377. Eng.2020, 8, 3995
Rh ₂ P/NPC		40		33	2	4	J. Mater.	Chem. A 2020, 8,25768
Ru-Ru ₂ P		43.4		35.1			10	J. Mater. Chem. A 2019,
Rh-Rh ₂ P@C		24		32	1	2	J. Mater.	Chem. A 2020, 8,12378 5621
RuP ₂ @PC		78.9		36.1			10	J. Mater. Chem. A 2021,
RhP _x @NPC		22		32	1	0	Adv. Fur 29,19017	nc9, Mater. 2019, 7902276
RuSe ₂ @NC		30		32			12	J. Mater. Chem. A 2022,
IrP ₂ @NPC		32		37	1	0	J. Mater.	Glogn634 2021, 9,2195
Rux R@3NB C/ GHSs		60. <u>@</u> 7		35.1 40	1	0	G arbon 2	20 AQ w! Matt4. 2023, 35, 2302007
Ru@1T-MoS ₂ MXene	-	42		38			160	Adv. Funct. Mater. 2023, 33,2212514