

Supplementary Information

Highly Bifunctional Rh₂P on N, P-Codoped Carbon for Hydrazine Oxidation Assisted Energy-Saving Hydrogen Production

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1. Experimental

1.1 Materials

$\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (99%) was purchased from Shanghai Energy Chemical. Adenosine 5'-monophosphate sodium salt (AMP) (98%) was purchased from Shanghai Aladdin Industrial Corporation. The commercial 20% Pt/C were provided by Shanghai Hesun Corporation. The 5% Nafion solution and Nafion 115 membrane were provided by Sigma-Aldrich Corporation.

1.2 Synthesis

1.2.1 The preparation of $\text{Rh}_2\text{P}/\text{NPC}$

$\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ and adenosine 5'-monophosphate sodium salt (AMP) were dissolved in 50 mL distilled water and stirred overnight. The obtained solution was dried in the oven at 80 °C after rotating evaporation. The obtained orange powder was pyrolyzed at 800 °C in Ar atmosphere for 1 hour. The black powder was washed three times in distilled water and dried at 80°C.

1.2.2 The preparation of Rh/C

50 mg preoxidized carbon black was sonicated in 15 mL water and then mixed with appropriate amounts of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, 10 mL NaBH_4 solution (the molar ratio of NaBH_4 and metal is 4:1) was added dropwise under vigorous stirring. The mixture was kept stirring for another 2 h followed by centrifuging thrice and drying.

1.2.3 The preparation of NPC

The metal-free N, P-codoped carbon (NPC) was obtained by the direct pyrolysis AMP at 800 °C in Ar atmosphere for 1h.

3. Physical characterizations

The morphology and structure were examined by the transmission electron microscope (TEM, Talos F200X G2), powder X-ray diffraction (XRD, SmartLab 9kW) and Raman spectrometer with an excitation wavelength of 532 nm (HORIBA iHR550). The high-resolution TEM and HAADF-STEM were recorded by JEM-ARM300F TEM/STEM with a spherical aberration corrector working at 300 kV. The componential information was obtained by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra spectrometer). The specific surface areas were extracted with nitrogen adsorption-

desorption isotherm (Micrometrics 2460) by the Brunauer-Emmett-Teller (BET) model at a pressure range of $P/P_0 = 0.05-0.3$, along with the Barrett-Joyner-Halenda (BJH) model for pore size distribution by the adsorption branch on isotherm. ICP-OES was performed with PerkinElmer Optima 8300.

4. Electrocatalytic experiments

The electrochemical station (Reference 3000, Gamry Instruments, USA) with a rotating disk electrode (RDE) system were used to conduct the electrochemical measurements. For the preparation of working electrode, the samples were initially ultrasonically dispersed into aqueous inks with the concentration of 2 mg mL^{-1} . $20 \text{ }\mu\text{L}$ of the catalyst ink was dropped onto a pre-prepared RDE with the diameter of 5 mm and dried at ambient condition, then $5 \text{ }\mu\text{L}$ of 0.5 wt. \% Nafion aqueous solution was added to increase the adherence. An Ag/AgCl/KCl (3.5 M) electrode and a platinum wire was selected as the reference and counter electrodes, the volume of 100 mL electrolyte was added into a 5-port electrolytic cell with N_2 gas inlet during the tests. The HER tests were performed in 1 M KOH while HzOR in 1 M KOH with $0.5 \text{ M N}_2\text{H}_4$. All the electrochemical data were treated with iR correction except for stability tests.

In the direct $\text{N}_2\text{H}_4/\text{H}_2\text{O}_2$ fuel cell (DHHPFC), the catalysts were loaded onto carbon paper (1 cm by 2 cm , 1 mg cm^{-2} , Sigracet 29BC), the anodes were the RuNi/C and commercial 20 wt. \% Pt/C catalysts, and their cathodes were all 20 wt. \% Pt/C . When testing the DHHPFCs, $5 \text{ M H}_2\text{O}_2$ in $0.5 \text{ M H}_2\text{SO}_4$ as the catholyte and $1 \text{ M N}_2\text{H}_4$ in 4 M KOH as the anolyte were flowed into the cell compartments with a flow rate of 5 mL min^{-1} by a two-channel peristaltic pump (EC200-01, Gaoss Union) connected with the silicone tube. The Nafion N115 membrane was used as the proton exchange membrane to separate two compartments.

The OHzS system driven by solar cell consists of three parts: a two-electrode OHzS unit with $\text{Rh}_2\text{P/NPC}$ as both anodic and cathodic catalysts and $0.5 \text{ M N}_2\text{H}_4$ in 1 M KOH as the electrolyte, a commercial polycrystalline silicon solar cell with rated voltage of 1.5 V and a Xe lamp. The polycrystalline silicon solar cell is illuminated by the 150 W ($15 \text{ V} \times 10 \text{ A}$) Xe lamp with light output power density of 2 Sun ($1 \text{ Sun} = 1000 \text{ W/m}^2$) and spectral output of $300 \text{ nm} \sim 2500 \text{ nm}$ (CEL-PF300-T9, Beijing China Education

Au-Light Co., Ltd).

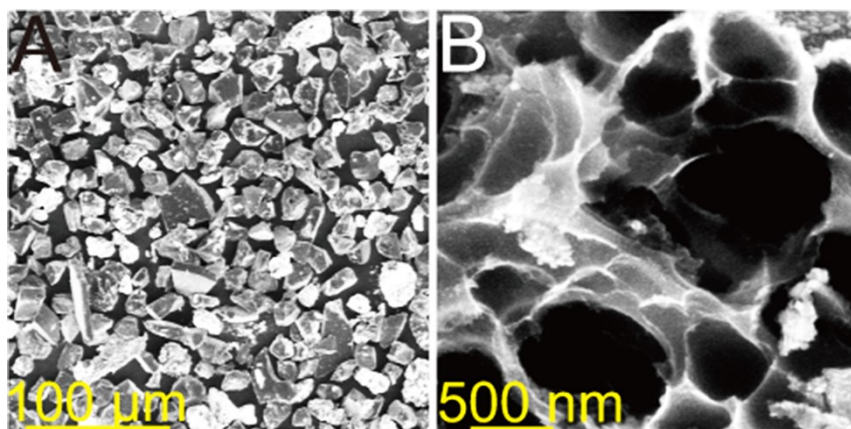


Fig. S1 SEM of Rh₂P/NPC.

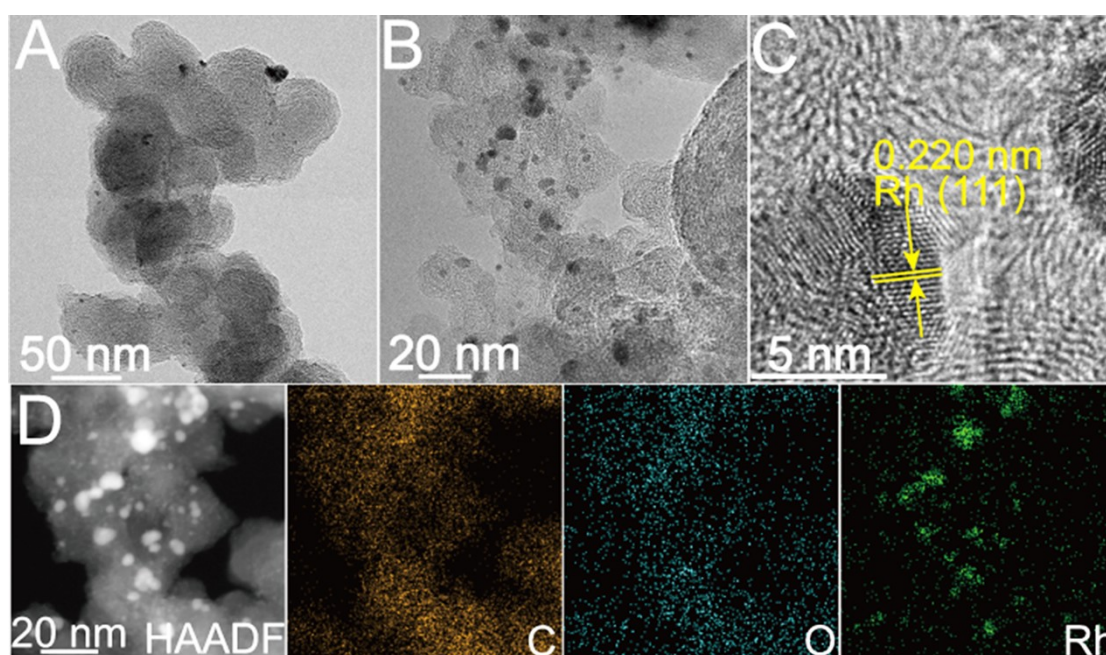


Fig. S2 (A-C) TEM images at different magnifications of Rh/C and (D) TEM HAADF and elemental mapping images of C, N, O and Ph of Rh/C.

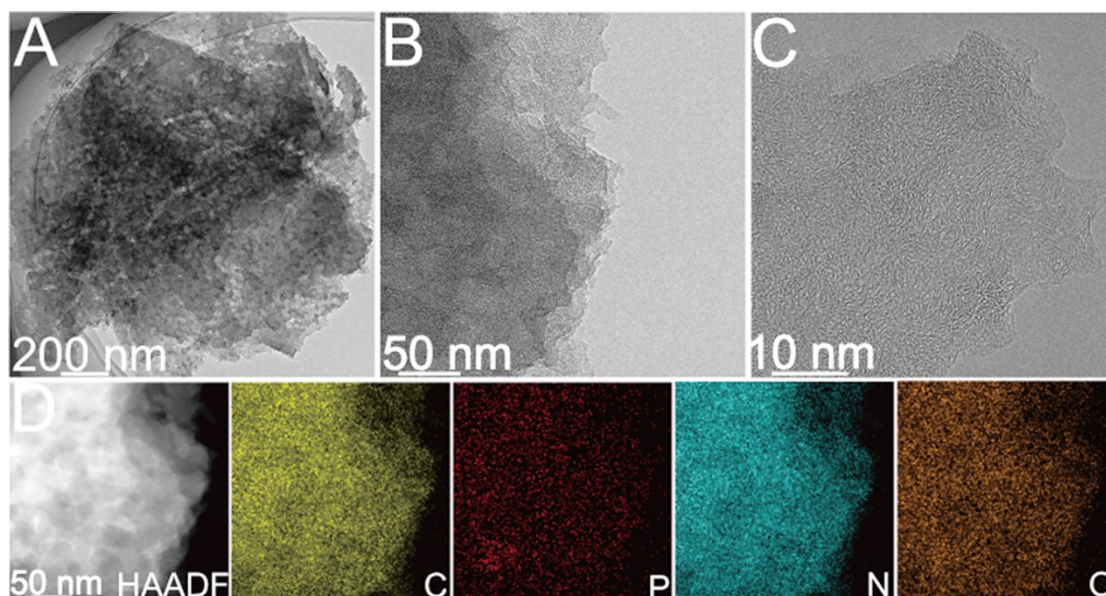


Fig. S3 (A-C) TEM images at different magnifications of NPC and (D) TEM HAADF and elemental mapping images of C, P, N and O of NPC.

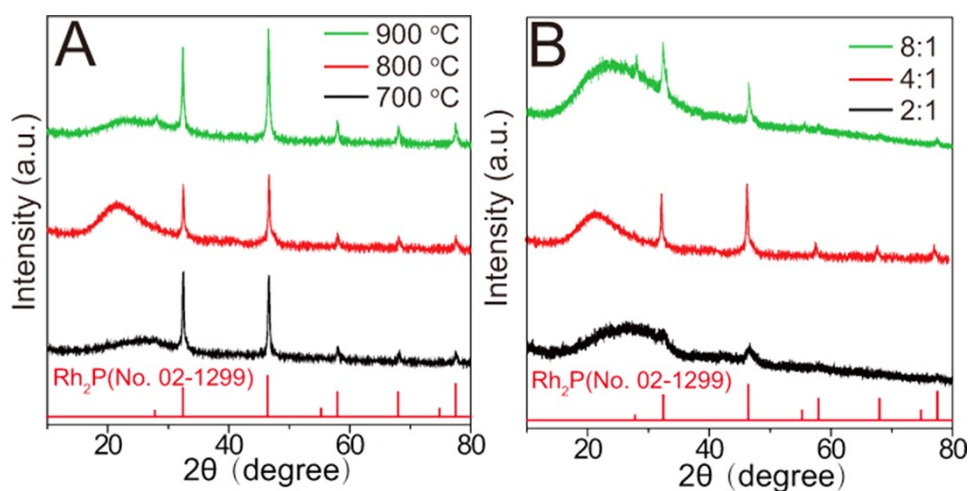


Fig. S4 The XRD patterns of the samples synthesized at different conditions. (A) different pyrolysis temperature, the molar ratio of AMP and RhCl_3 is 4:1, (B) different molar ratio of AMP and RhCl_3 with the pyrolysis temperature at 800 °C.

As shown in Figure S1, different preparation conditions have been examined including the molar ratio of AMP and RhCl_3 and pyrolysis temperature. XRD patterns confirm the pure Rh_2P component can be formed at all conditions. According to the electrocatalytic performance of abovementioned samples, the optimal preparation conditions were selected as following: the molar ratio of AMP and RhCl_3 is 4:1, the pyrolysis temperature is 800 °C.

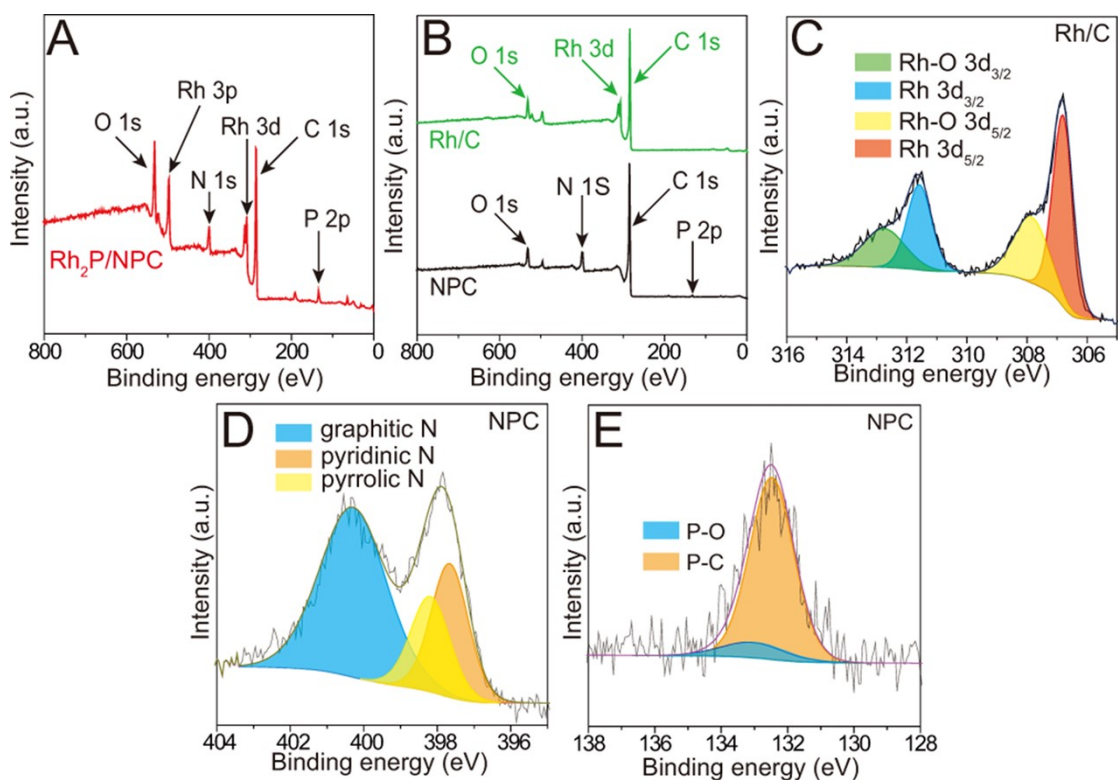


Fig. S5 (A) XPS survey scan of $\text{Rh}_2\text{P}/\text{NPC}$, Rh/C and NPC . The high-resolution XPS spectra of (B) Rh 3d of Rh/C , (C) N 1s of NPC , (D) P 2p of NPC .

For NPC , the high-resolution N 1s spectrum can be also divided into three subpeaks around 397.66, 398.19 and 400.29 eV, corresponding to pyridinic, pyrrolic and graphitic N species, respectively. The P 2p spectra can be fitted into two peaks centered in 132.48 and 133.05 eV, attributing to the $\text{P}-\text{C}$ and $\text{P}-\text{O}$ bonds.

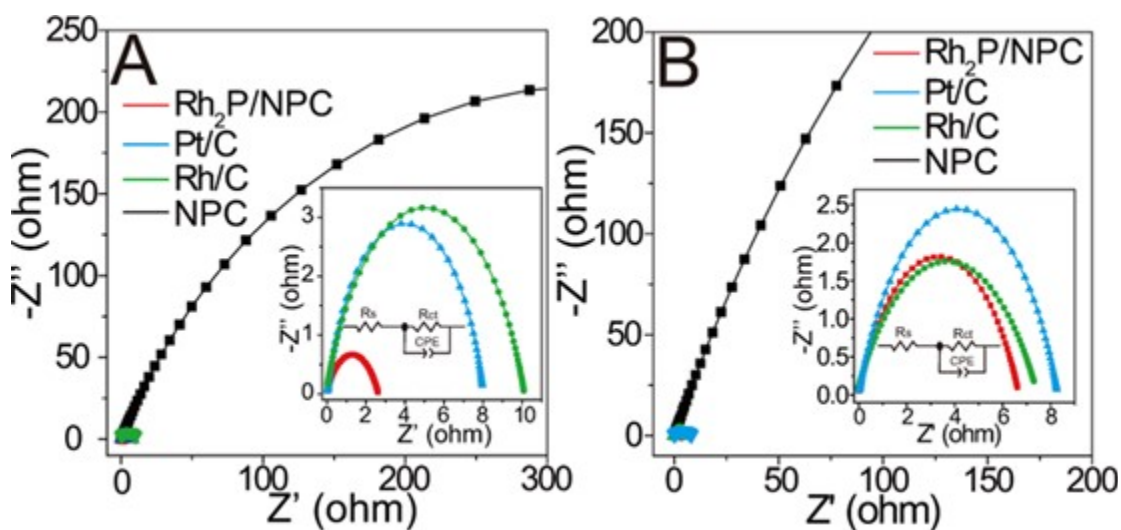


Fig. S6 (A) The electrochemical impedance spectra of (A) HER in 1 M KOH and HzOR

in 1 M KOH+0.5 M N₂H₄.

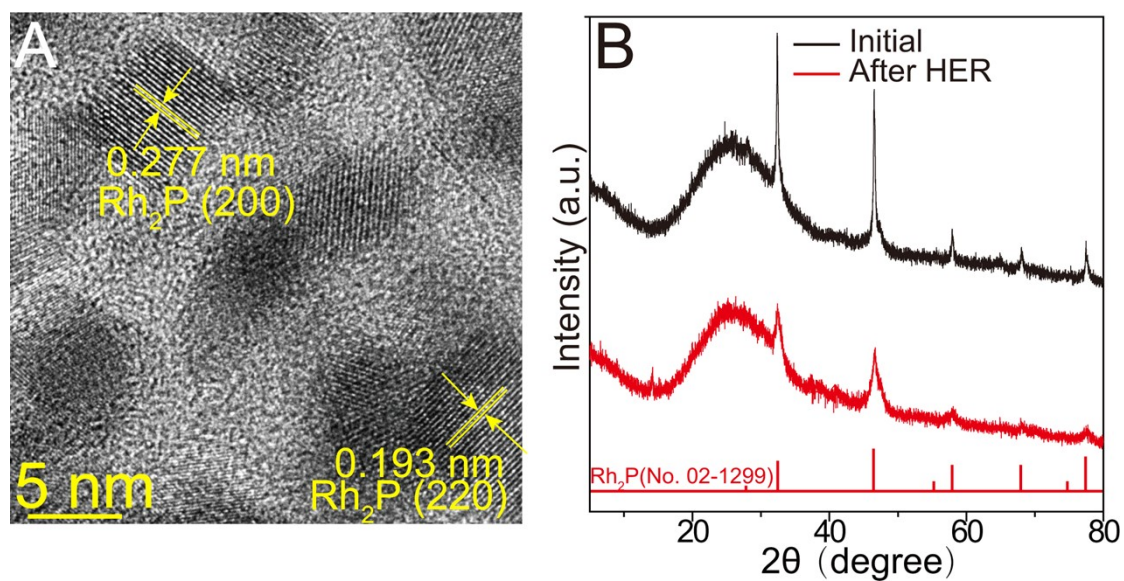


Figure S7. (A) The TEM image and (B) XRD pattern of Rh₂P/NPC collected from HER electrode after long-time stability test in alkaline OHzS cell.

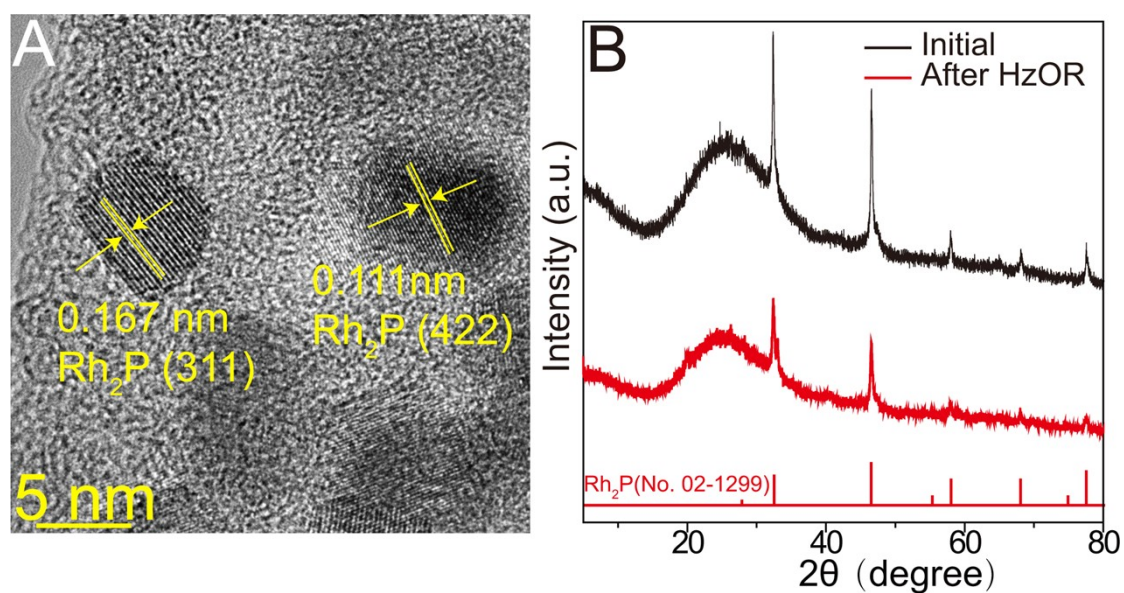


Figure S8. (A) The TEM image and (B) XRD pattern of Rh₂P/NPC collected from HzOR electrode after long-time stability test in alkaline OHzS cell.

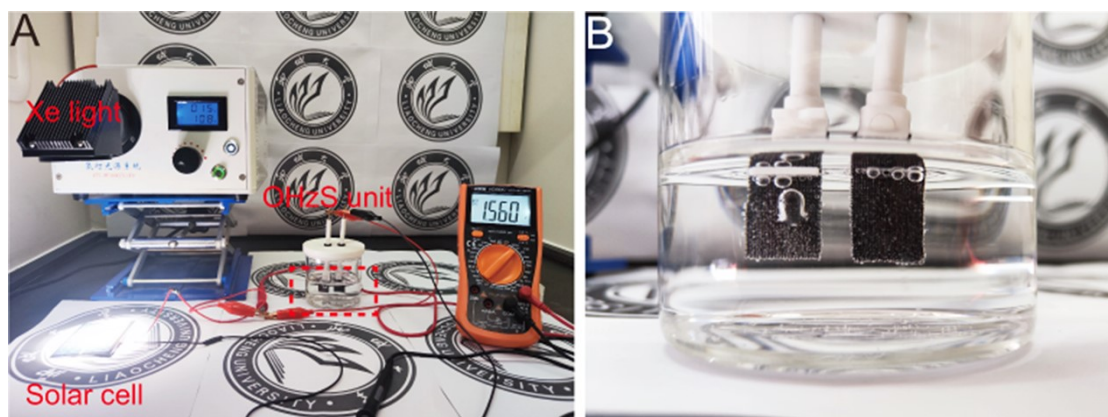


Fig. S9 (A) Digital photograph of the assembled solar cell-powered OHzS cell, (B) digital photograph of the evolution of gas bubbles on the solar cell-powered OHzS cell.

Table S1. The BET surface area, pore volume and pore diameter of different samples.

Samples	BET surface area (m²/g)	Pore volume (cm³/g)	Pore diameter (nm)
Rh₂P/NPC	178.86	0.12	4.72
Rh/C	92.65	0.26	14.57
NPC	381.44	0.55	8.85

Table S2. Quantitative XPS information of different samples.

Samples	Rh (at%)			P (at%)				N (at%)				
	Total Rh	Rh	Rh-O	Total P	P-Rh	P-C	P-O	Total N	Pyridinic N	Pyrolic N	Graphitic N	Oxidized N
Rh ₂ P/NPC	1.33	0.96	0.37	6.19	1.26	3.24	1.69	4.81	1.89	1.81	0.70	0.41
Rh/C	2.69	1.66	1.03									
NPC				0.89		0.79	0.10	10.86	2.70	2.02	6.14	