

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

RuP₂-based hybrids derived from MOFs: highly efficient pH-universal electrocatalysts for hydrogen evolution reaction

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S1. Figures in Supporting Information

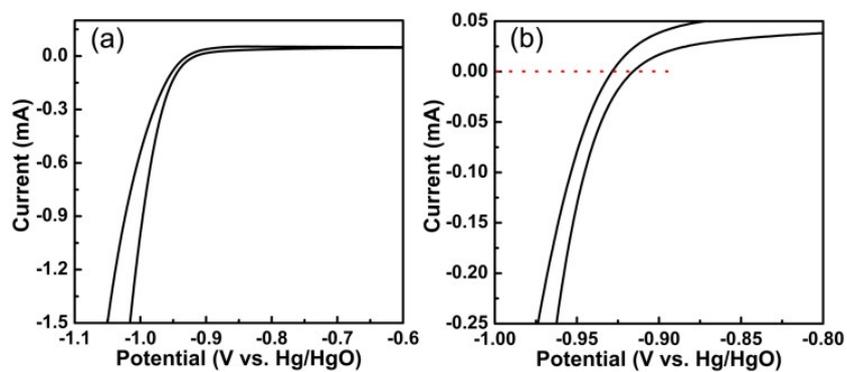


Fig. S1 (a) CV curve of Hg/HgO electrode calibration in 1.0 M KOH and (b) The enlarged view of (a).

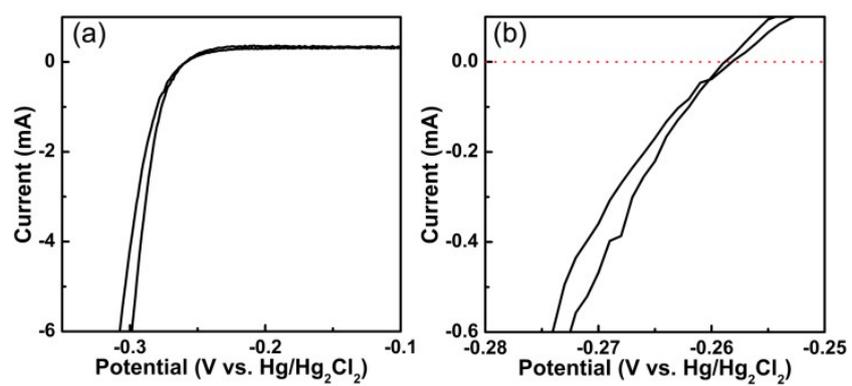


Fig. S2 (a) CV curve of Hg/Hg₂Cl₂ electrode calibration in 0.5 M H₂SO₄ and (b) The enlarged view of (a).

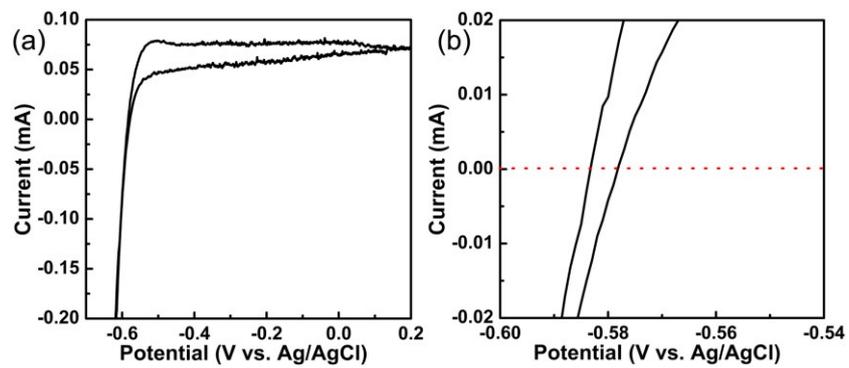


Fig. S3 (a) CV curve of Ag/AgCl electrode calibration in 1.0 M PBS and (b) The enlarged view of (a).

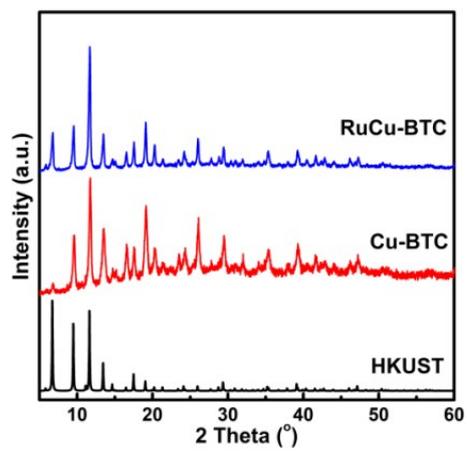


Fig. S4. PXRD patterns of MOF precursors.

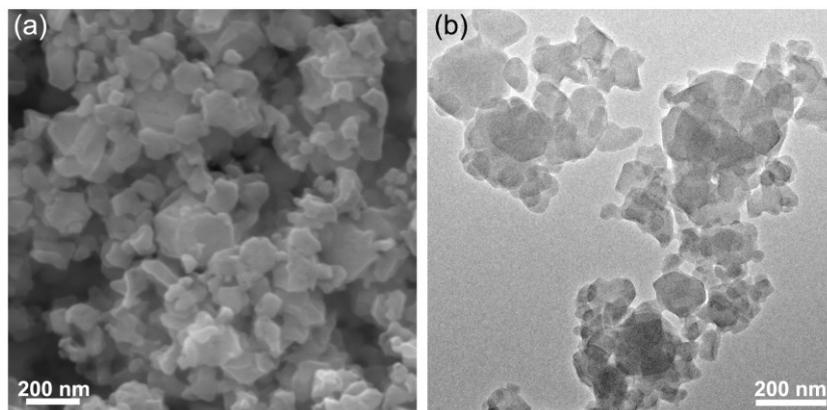


Fig. S5 (a) SEM and (b) TEM images of Cu-BTC.

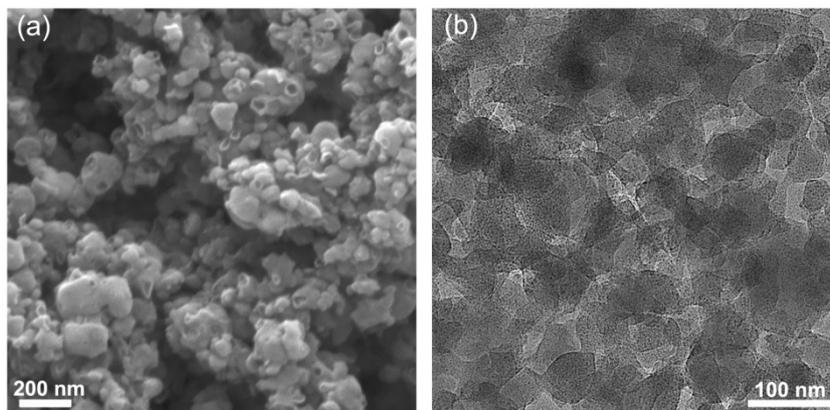


Fig. S6 (a) SEM and (b) TEM images of RuCu-BTC.

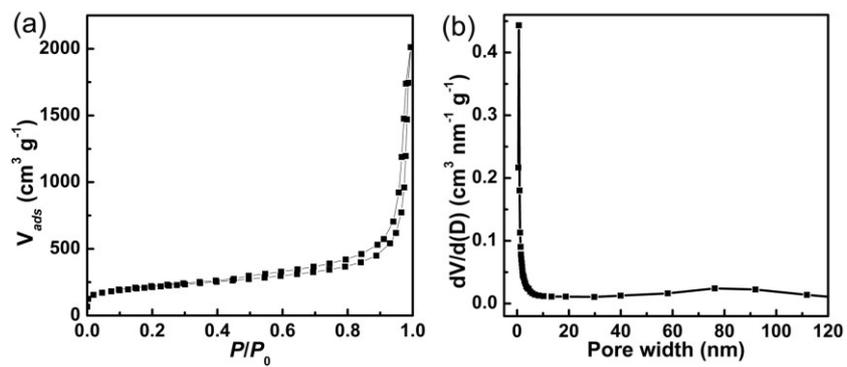


Fig. S7 (a) N_2 sorption isotherm of RuP₂@PC and (b) corresponding pore size distribution calculated using NLDFT method.

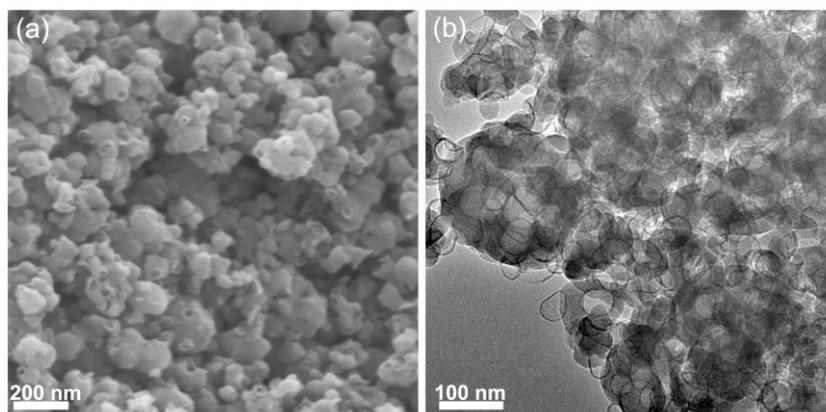


Fig. S8 (a) SEM and (b) TEM images of PC.

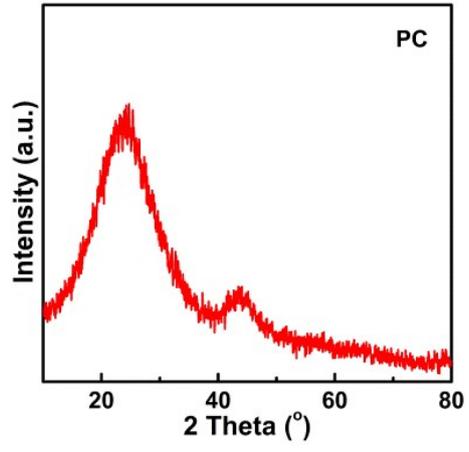


Fig. S9 PXRD pattern of PC.

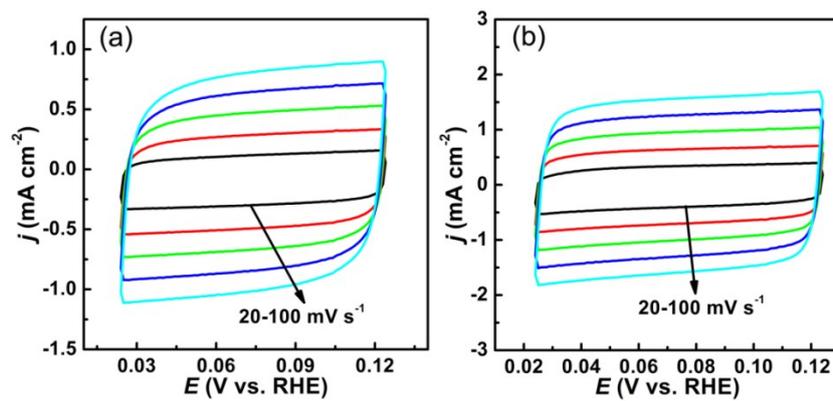


Fig. S10 CV curves of PC and RuP₂@PC in the non-Faradaic potential region recorded at different scan rates in 1.0 M KOH.

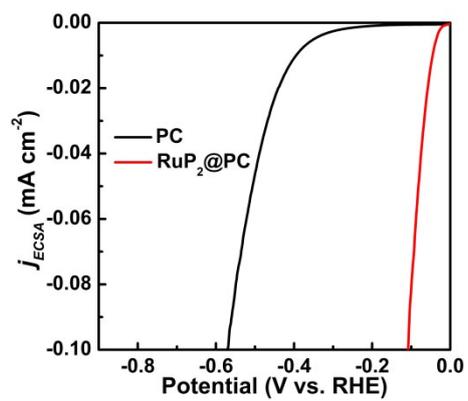


Fig. S11 ECSA-normalized HER polarization curves for RuP₂@PC in 1.0 M KOH.

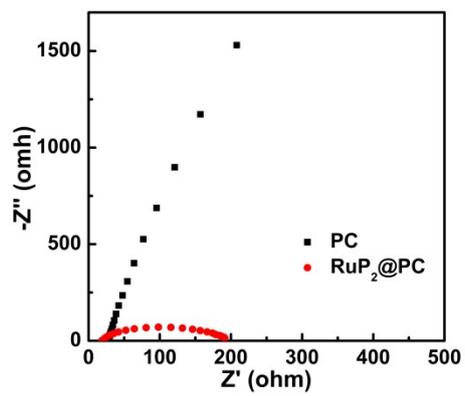


Fig. S12 The EIS plots of PC and RuP₂@PC in 1.0 M KOH at -156 mV vs RHE.

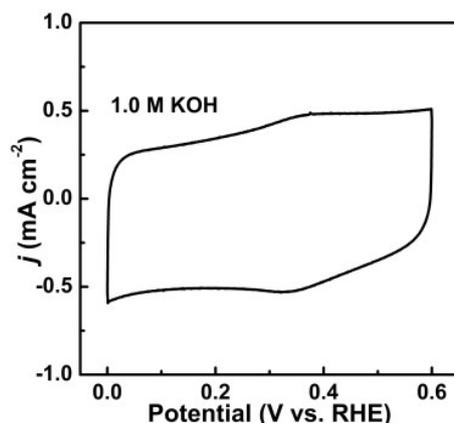


Fig. S13 CV curve measured in 1.0 M KOH for RuP₂@PC.

The evaluation of TOF

The calculation method of TOF values is according to the following equation:

$$\text{TOF} = \frac{j}{2Fn} \quad (1)$$

where j is the measured current density (mA cm^{-2}) for the HER, F is the Faraday constant (96485 C mol^{-1}) and n is the number of active sites (mol cm^{-2}). The factor $1/2$ is shown because two electrons are needed to generate one hydrogen molecule. The number of active sites is achieved according to cyclic voltammograms (CV) method. Specifically, the CV curves are investigated in 1.0 M KOH, 0.5 M H_2SO_4 , and 1.0 M PBS solution with the potential window range from 0 V to 0.6 V vs RHE at 50 mV s^{-1} . Then, by integrating each CV curve's charge over the whole potential range, the half value of the charge was obtained, which is the value of the surface charge density (Q_s).

$$Q_s = Fn \quad (2)$$

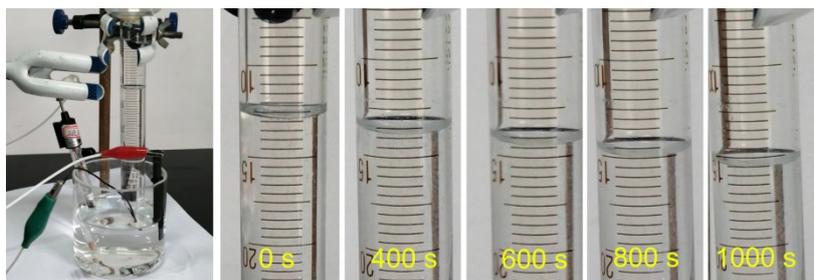


Fig. S14 Gas collection device for HER and photographs of hydrogen collected at different time in 1.0 M KOH.

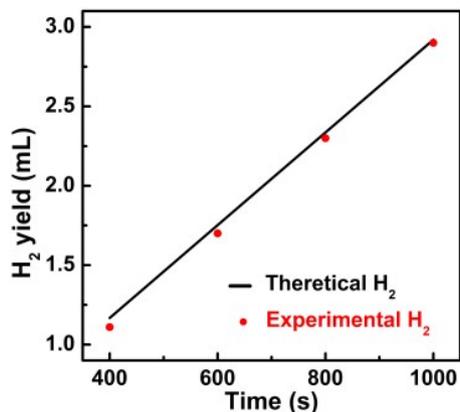


Fig. S15 Theoretically calculated and experimentally measured amount of hydrogen versus time for RuP₂@PC in 1.0 M KOH.

To estimate the faradaic efficiency (FE), a gas collection device was employed for the experiment (Fig. S14). The as-prepared catalyst (4 mg) was dispersed in the mixture of 1940 μL ethanol solution and 40 μL nafion solution (5 wt%) by continuous sonication for 30 min. Then, the ink was coated onto the carbon cloth ($1 \times 1 \text{ cm}^2$), which was used as the working electrode. A constant current density (23 mA cm^{-2}) was applied on the working and the volume of the evolved gas was recorded synchronously. Thus, the FE is estimated from the observed gas volume and the theoretical gas volume calculated by the charge passed through the electrode. The related formula is as follows: $\text{FE} = V_{\text{experimental}} / [V_m \times Q / (NF)]$, where the N is the number of transferred electrons, F is the faraday constant (96485 C mol^{-1}), Q is the charge passed through the electrode, and V_m is the gas molar volume at 298 K and 101 kPa (24.5 L mol^{-1}). As shown Fig. S15, the faradaic efficiency of RuP₂@PC for the HER is calculated to be 97.8%.

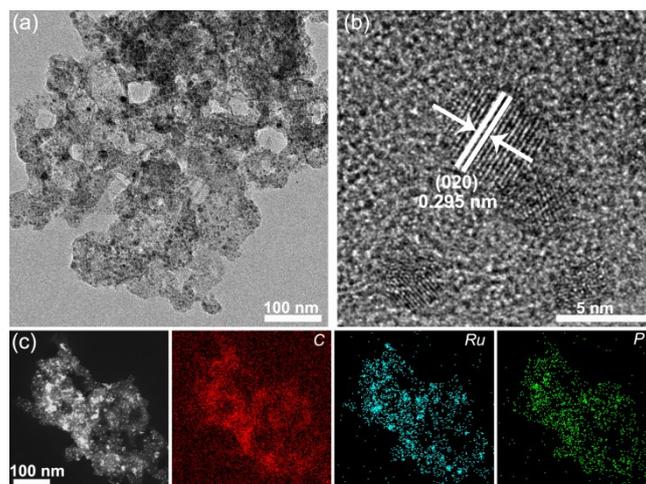


Fig. S16 (a) TEM, (b) HRTEM, and (c) STEM and EDX elemental mapping images for C, P, and Ru in RuP₂@PC after stability test.

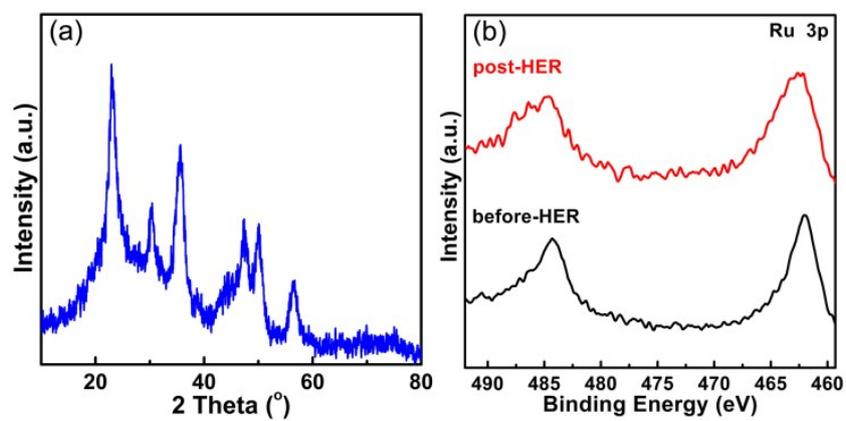


Fig. S17 (a) PXRD pattern of RuP₂@PC after HER test in 1.0 M KOH. (b) Ru 3p for RuP₂@PC before and after HER test in 1.0 M KOH.

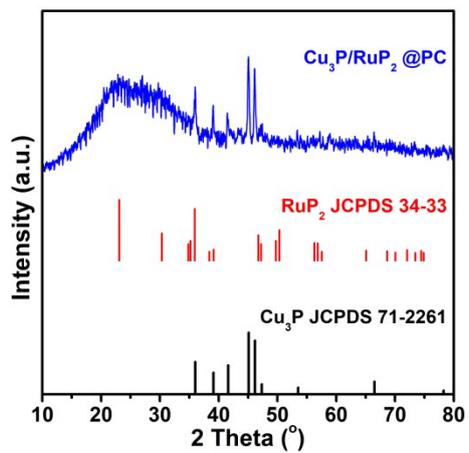


Fig. S18 PXRD pattern of $\text{Cu}_3\text{P}/\text{RuP}_2@\text{PC}$.

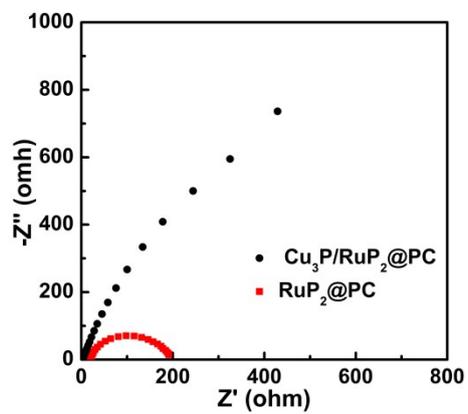


Fig. S19 The EIS plots of RuP₂@PC and Cu₃P/RuP₂@PC in 1.0 M KOH at -156 mV vs RHE.

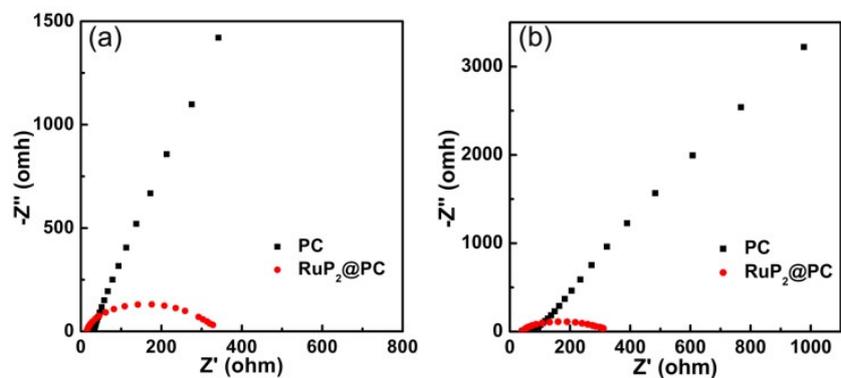


Fig. S20 The EIS plots of PC and RuP₂@PC in 0.5 M H₂SO₄ at -29.2 mV vs RHE and 1.0 M PBS at -69.3 mV vs RHE, respectively.

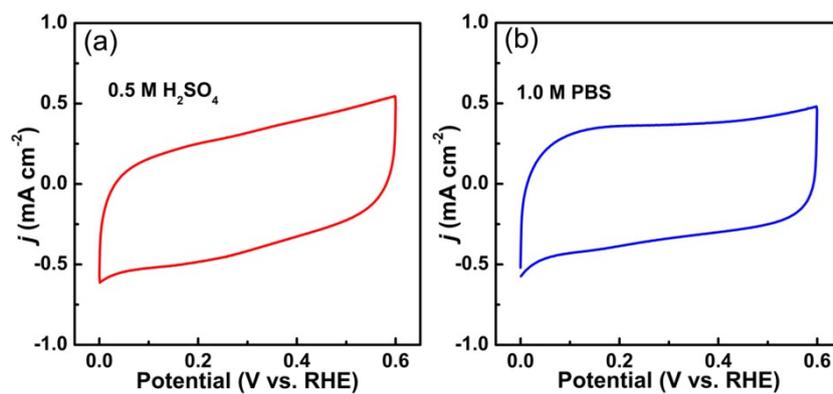


Fig. S21 CV curves for RuP₂@PC measured in 0.5 M H₂SO₄ and 1.0 M PBS.

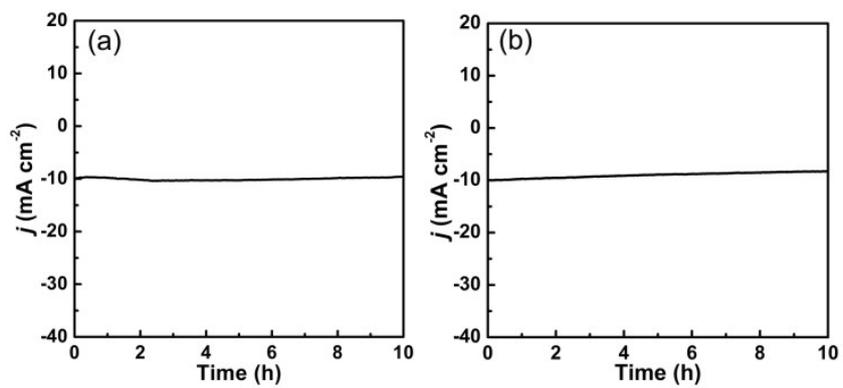


Fig. S22 I-t curves of RuP₂@PC in 0.5 M H₂SO₄ (a) and (b) 1.0 M PBS solution.

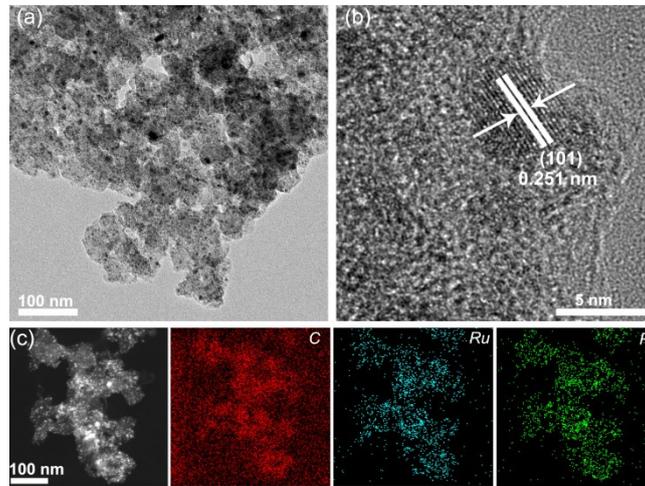


Fig. S23 (a) TEM, (b) HRTEM, and (c) STEM and EDX elemental mapping images for C, P, and Ru in RuP₂@PC after HER test in 0.5 M H₂SO₄.

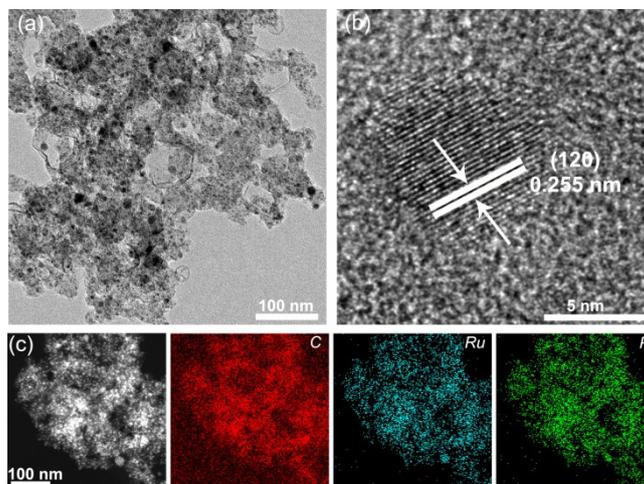


Fig. S24 (a) TEM, (b) HRTEM, and (c) STEM and EDX elemental mapping images for C, P, and Ru in RuP₂@PC after HER test in 1.0 M PBS.

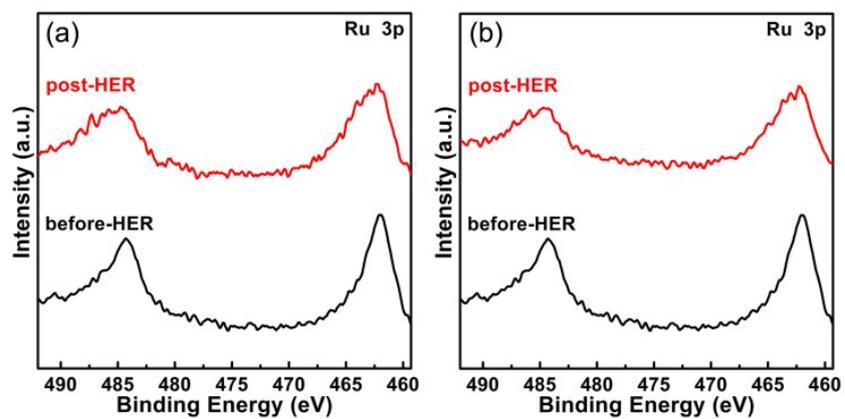


Fig. S25 Ru 3p for RuP₂@PC before and after HER test in 0.5 M H₂SO₄ (a) and 1.0 M PBS (b).

S2. Table in Supporting Information

Table S1. Comparison of catalytic performance of RuP₂@PC and other reported materials toward HER in alkaline, acidic, and neutral conditions.

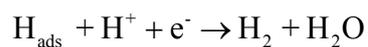
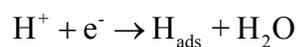
Catalysts	Tafel slope [mV dec ⁻¹]	η_{10} (mV)	Electrolyte solution	References
RuP ₂ @PC	36.7	78.9	1.0 M KOH	This work
	35.1	60.6	0.5 M H ₂ SO ₄	
	66.8	113.1	1.0 M PBS	
RuP ₂ / 1.03CDs-900	63.29	26	1.0 M KOH	<i>ACS Sustainable Chem. Eng.</i> 2020 , 8, 3995–4002.
	61.3	~100	0.5 M H ₂ SO ₄	
	--	--	1.0 M PBS	
NFP/C-3	72	95	1.0 M KOH	<i>Sci. Adv.</i> 2019 , 5, eaav6009.
	54	72	0.5 M H ₂ SO ₄	
	70	117	1.0 M PBS	
Ru ₂ P	43	57	1.0 M KOH	<i>Chem. Commun.</i> 2019 , 55, 7828.
	101	---	0.5 M H ₂ SO ₄	
	---	~210	1.0 M PBS	
RuP ₂ /CNT	65	40	1.0 M KOH	<i>Chem. Eur.J.</i> 2019 , 25, 8579.
	57	58	0.5 M H ₂ SO ₄	
	82	109	1.0 M PBS	
MoP/CNTs-700	73	86	1.0 M KOH	<i>Adv. Funct. Mater.</i> 2018 , 28, 1706523
	60	83	0.5 M H ₂ SO ₄	
	115	102	1.0 M PBS	
L-RP/C	34	18	1.0 M KOH	<i>Adv. Mater.</i> 2018 , 30, 1800047.
	37	19	0.5 M H ₂ SO ₄	
	37	95	1.0 M PBS	
RuP ₂ @NPC	69	52	1.0 M KOH	<i>Angew. Chem. Int. Ed.</i> 2017 , 129, 11717.
	38	38	0.5 M H ₂ SO ₄	
	87	57	1.0 M PBS	
CoP@BCN	52	215	1.0 M KOH	<i>Adv. Energy Mater.</i> 2017 , 7, 1601671.
	46	87	0.5 M H ₂ SO ₄	
	59	122	1.0 M PBS	

S3. Note in Supporting Information

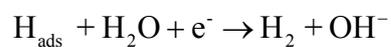
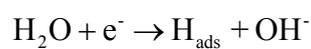
Note 1.

The HER process can be described using the following elementary steps:

under acidic condition:



under alkaline condition:



Under acidic condition, hydrogen ions (protons) directly combine with an electron and then are chemically adsorbed on the surface of the electrocatalysts, forming H_{ads} , whereas in alkaline solutions, the hydrogen ions are from the cleaved water molecules.