Supporting Information

Experimental

Materials. Ruthenium chloride, sodium hypophosphite, carbon support (XC72), absolute ethyl alcohol were all gained from Aladdin. 20%Pt/C was purchased from Alfa Aesar. No further purification was taken before use.

Preparation of Ru-Ru_2P/PC catalysts. Certain amount XC-72 carbon support, $RuCl_3$ and $NaH_2PO_2 \cdot H_2O$ (with various Ru:P ratios) were added in the beaker and 30 ml anhydrous ethanol was added and stirred at room temperature until the solvent was evaporated. Mass weight of NaH_2PO_2 was controlled to be 10.9 mg to control the pressure (1.96 MPa) in reactor during the high-pressure synthesis. After drying at 70 ^{o}C overnight, the powder was transferred into the high-pressure reaction kettle, which was made from stainless steel with the inside surface pre-carbonized by melamine, in the glove box under Ar atmosphere. Subsequently, the reaction kettle was put into the tube furnace to be calcined at 300 ^{o}C for 2h with a temperature increasing rate of 2 ^{o}C/min under nitrogen. After cooling to room temperature, the product was washed with deionized water for several times and dried overnight. PC catalyst was prepared from 100 mg XC72 and 10.9 mg NaH_2PO_2 following the same procedure. *Preparation of Ru/C catalyst*. 50 mg XC72, 60 mL glycol and 40 mL deionized water mixed in a three-neck flask and ultrasonically dispersed for 30 minutes. 11 mg ruthenium trichloride was subsequently added to the mixture and stirred for 20 min. The reaction was then refluxed at 140 °C for 6 h and the product was washed by ethanol and deionized water repeatedly before dried at 60 °C overnight. [1]

Electrochemical measurements. All the electrochemical measurements, including cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) assessments were carried out on Gamry (Interface 1000E, USA) electrochemical workstation with a standard three-electrode system configuration. Typically, 4 mg commercial 20% Pt/C, homemade Ru/C or as-fabricated Ru-Ru_2P/PC catalysts were dispersed in 600 μL of deionized water, 400 μL of ethanol and 12 μL of Nafion solution (5 wt.%) by ultrasonic treatment for 1 h to obtain homogeneous suspension. Thereafter, 5 μL of the resultant ink (containing 20 μg of catalyst) was pipetted on the surface of glassy carbon (GC) electrode with a diameter of 3 mm and then air-dried to achieve a catalyst mass loading of 0.285 mg/cm^2. LSV at a scan rate of 2 mV/s was performed in N_2-saturated 0.5 M H_2SO_4/1M KOH electrolyte employing GC casted with varied catalysts as the working electrode, graphite rod as the counter electrode, saturated calomel electrode (SCE, acidic condition) and Hg/HgO electrode (alkaline condition) as the reference electrode. The GC working electrode with coated catalyst underwent a cyclic voltammetry (CV) cycled between -0.10 to 0.20 V for 6 cycles prior to the LSV evaluation. CV cycles between -0.2 and 0.2 V were conducted at 50 mV/s to investigate the cycling stability of the catalysts. Electrochemical impedance spectroscopy (EIS) analysis was executed over the frequency range from 1 MHz to 0.1 Hz with an applied perturbation voltage value of 5 mV as the excitation AC amplitude and DC voltage biased at a cathodic overpotentials at 10 mA/cm^2 (η_{10}) and 20 mA/cm^2 (η_{20}). For the chronoamperometric (I-t) stability examination, the working electrode was biased at η=100 mV in alkaline

media (1M KOH) for 10 h. All of the potentials mentioned in this study were referenced to a reversible hydrogen electrode (RHE).

Characterizations. The crystal phase of synthesized powder was detected by X-ray diffraction (XRD, Bruker AXS D8-Focus, Germany) with Cu Kα radiation in the range of 2θ from 10 ^{o} to 90 ^{o}. The micromorphology and elemental distribution of Ru-Ru_2P/PC catalyst was observed by means of a field emission scanning electron microscopy (FESEM, Hitch SU8010, Japan) and a high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F30; Thermo Fisher Titan Themis G2) equipped with an energy-dispersive X-ray Spectroscope (EDS, Oxford INCA x-sight, England). The X-ray photoelectron spectroscopy (XPS, Escalab 250XI, ThermoFisher, USA) was employed to further explore the composition and chemical environment of the samples. The thermogravimetry (TG, Netzsch STA 409 PC, Germany) was conducted under atmospheric conditions at a heating ramp of 10 ^{o}C/min from ambient temperature to 800 °C. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method applied to N_2 adsorption isotherm measurement utilizing a MicroActive for ASAP 2460 (Micromeritics Instrument Corporation).

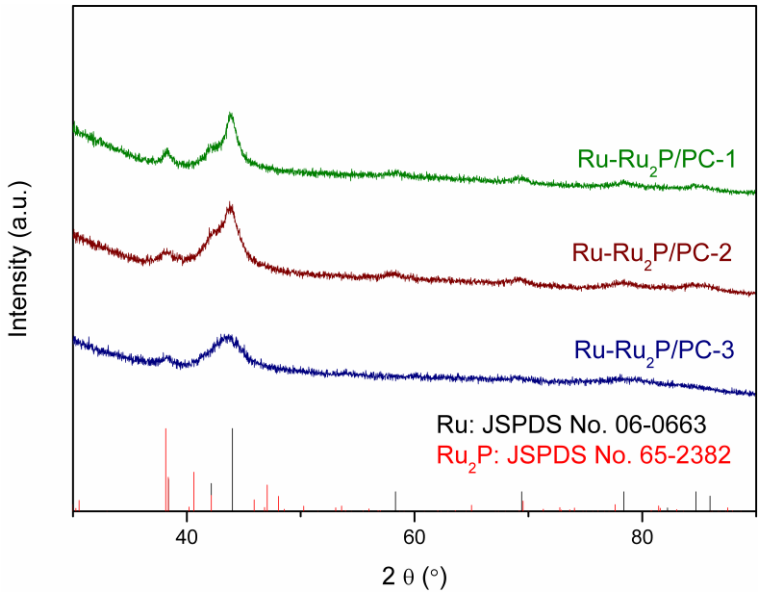


Figure S1. XRD patterns of the Ru-Ru_2P/PC-1, Ru-Ru_2P/PC-2 and Ru-Ru_2P/PC-3 catalysts.

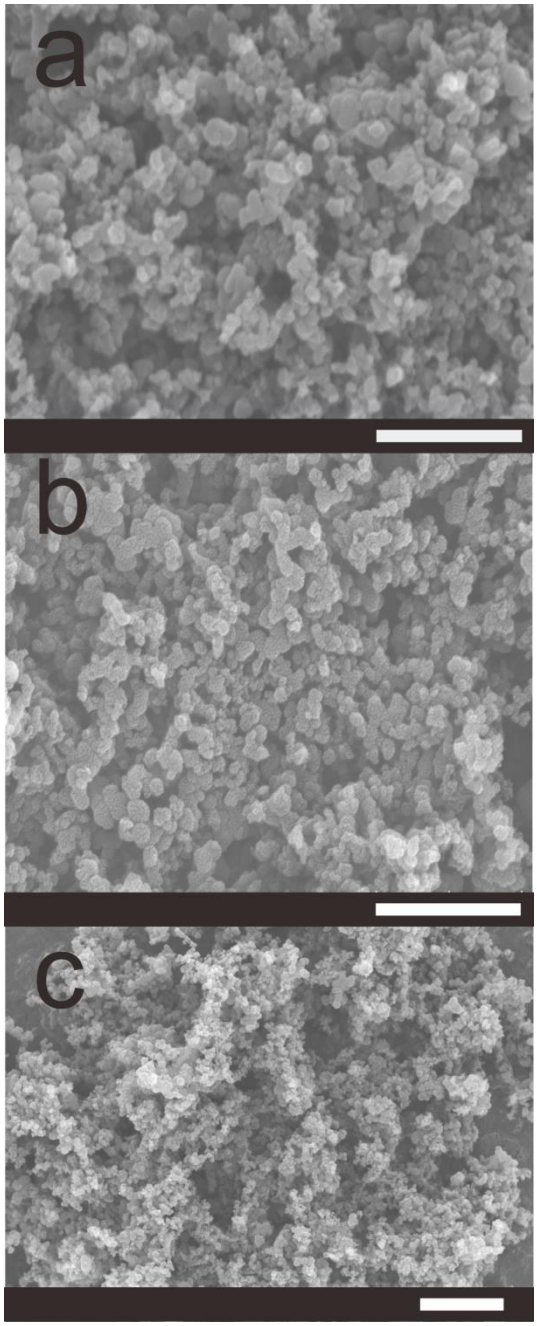


Figure S2. SEM images of (a) Ru-Ru_2P/PC-1, (b) Ru-Ru_2P/PC-3 and (c) the pristine carbon support.

(scale bar: 1 μm)

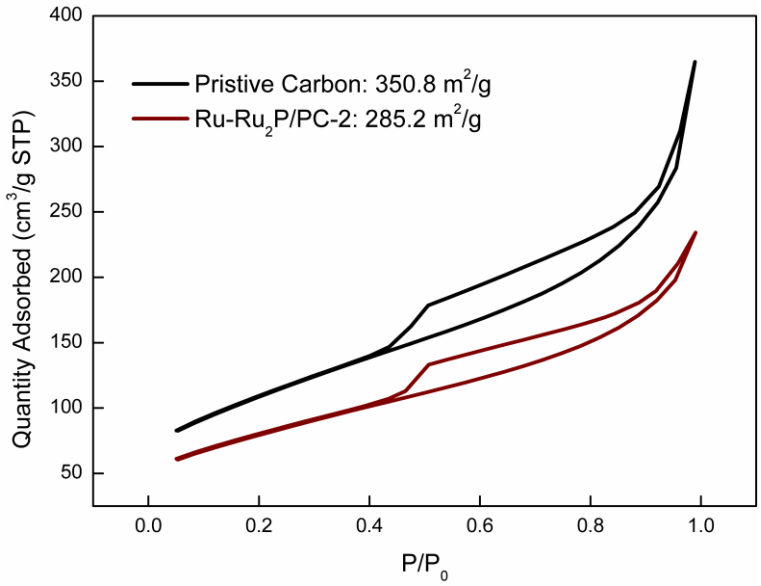


Figure S3. N_2 sorption isotherm of the Ru-Ru_2P/PC-2 catalyst and the pristine XC-72R active carbon support.

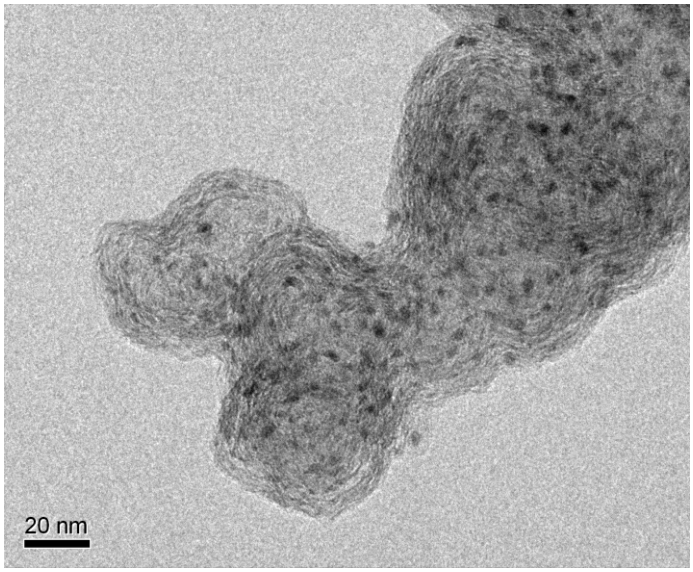
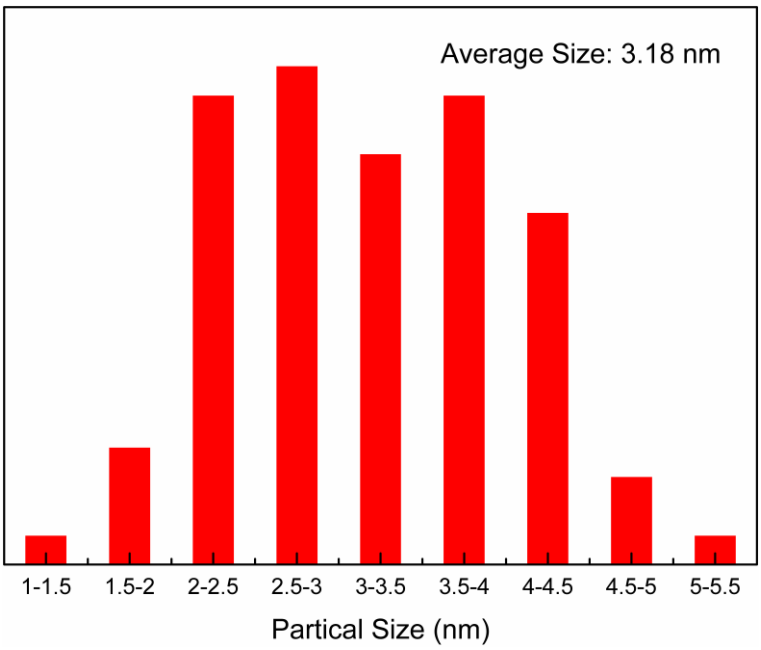


Figure S4. TEM image of the Ru-RuP/PC-2 catalyst.



FigureS5. Statistical size distribution of the nano-particles in Figures 1c and S4.

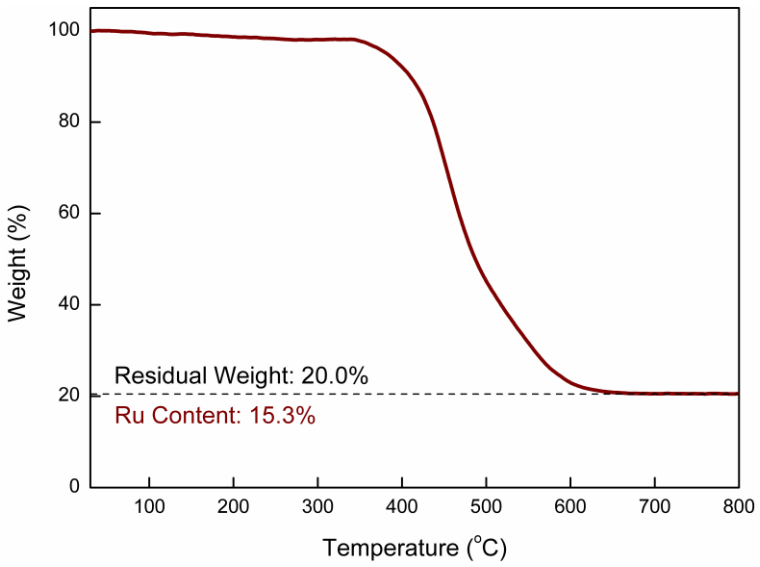


Figure S6. TG curve of the Ru-Ru_2P/PC-3 catalyst measured in O_2 atmosphere.

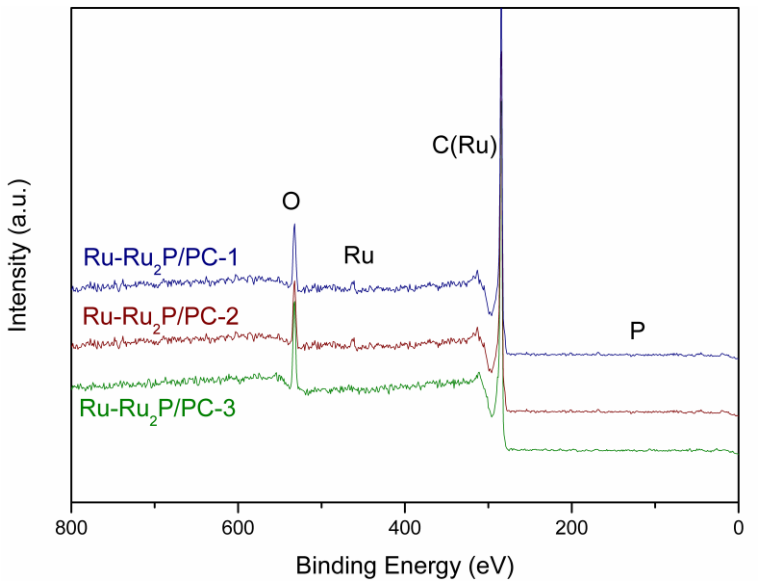


Figure S7. XPS survey spectrum for the Ru-Ru_2P/PC catalysts.

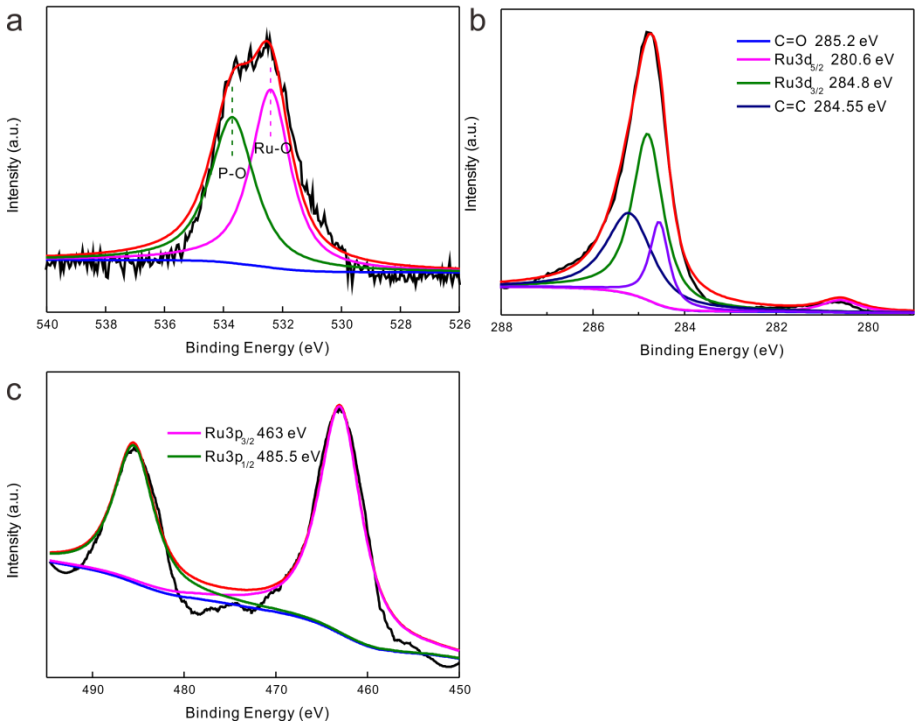


Figure S8. High resolution (a) O 1s, (b) Ru 3d and (c) Ru 3p XPS spectra of the Ru-Ru_2P/PC-2 catalyst.

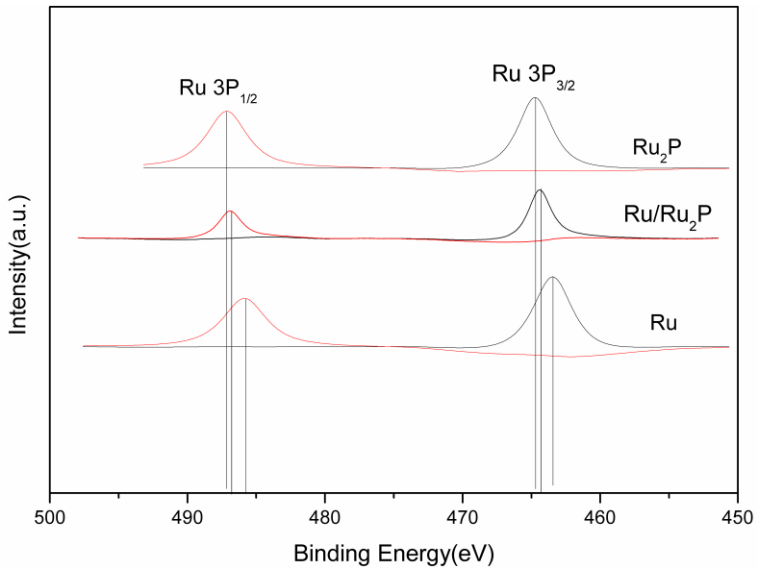


Figure S9. High resolution Ru 3p XPS spectra of the Ru_2P, Ru and Ru-Ru_2P/PC-2.

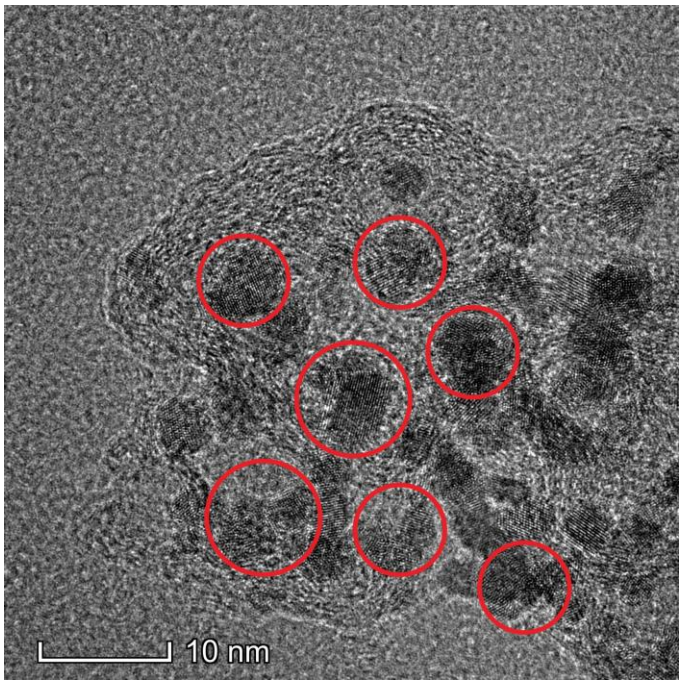


Figure S10. HR-TEM image of the Ru-Ru_2P/PC catalyst to evaluate the well construction of Ru/Ru_2P interfaces.

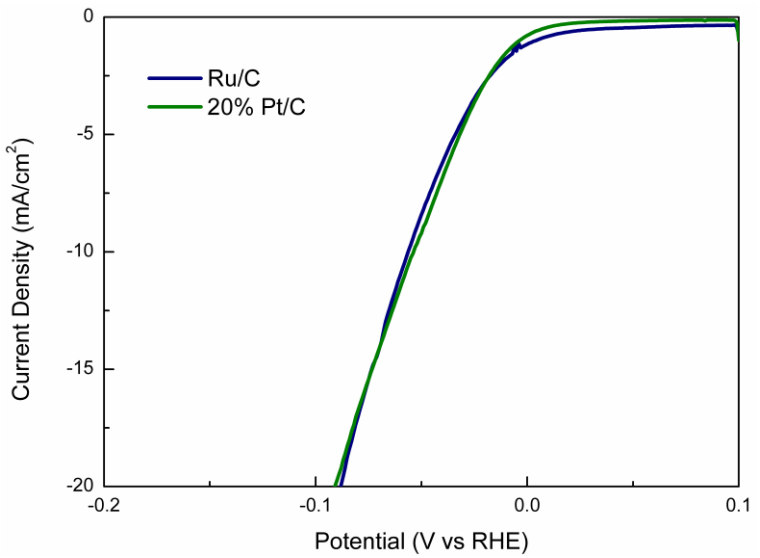


Figure S11. LSV curves of the Ru/C catalyst and the commercial Pt/C catalyst in 1 M KOH solution.

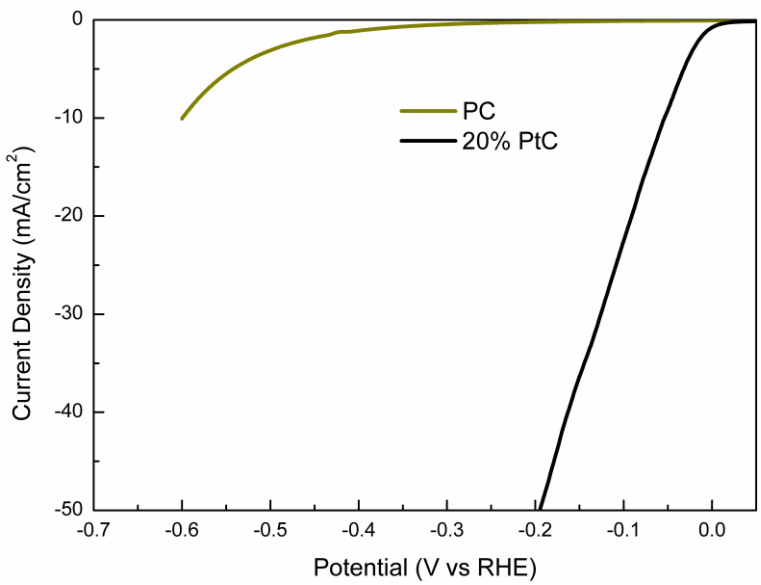


Figure S12. LSV curves of the PC catalyst and the commercial Pt/C catalyst in 1 M KOH solution.

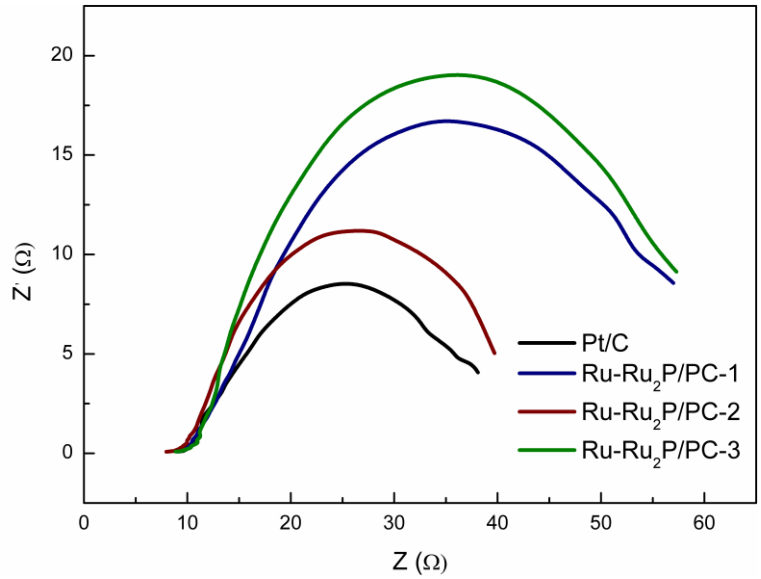


Figure S13. EIS curves recorded at η_{10} of the Ru-Ru_2P/PC catalyst and the commercial Pt/C catalyst.

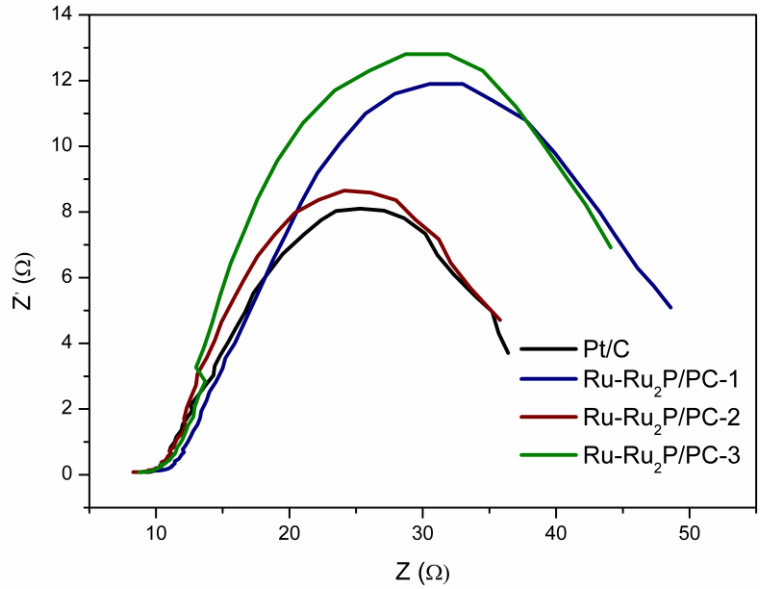


Figure S14. EIS curves recorded at η_{20} of the Ru-Ru_2P/PC catalyst and the commercial Pt/C catalyst.

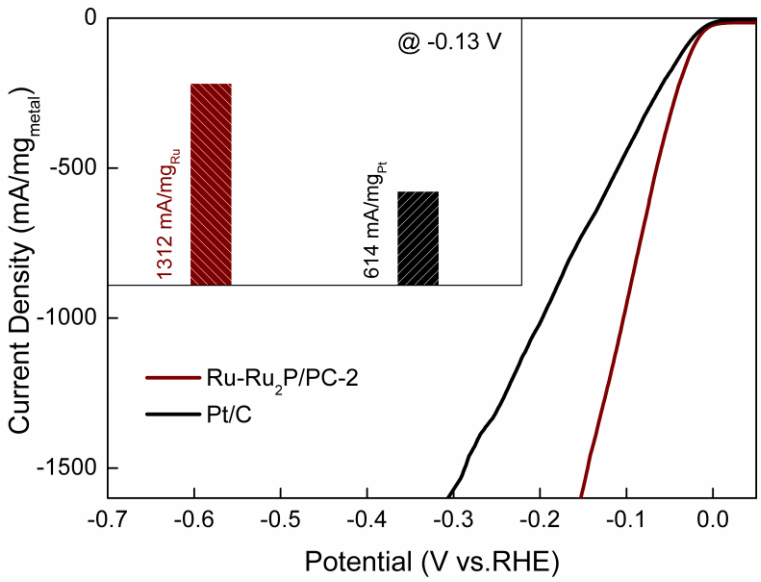


Figure S15. Mass alkaline HER activity of the Ru@RuP/PC-2 catalyst and the commercial Pt/C catalyst by considering the noble metal loading measured in 1 M KOH. (inset: mass normalized HER current density at overpotential of 130 mV)

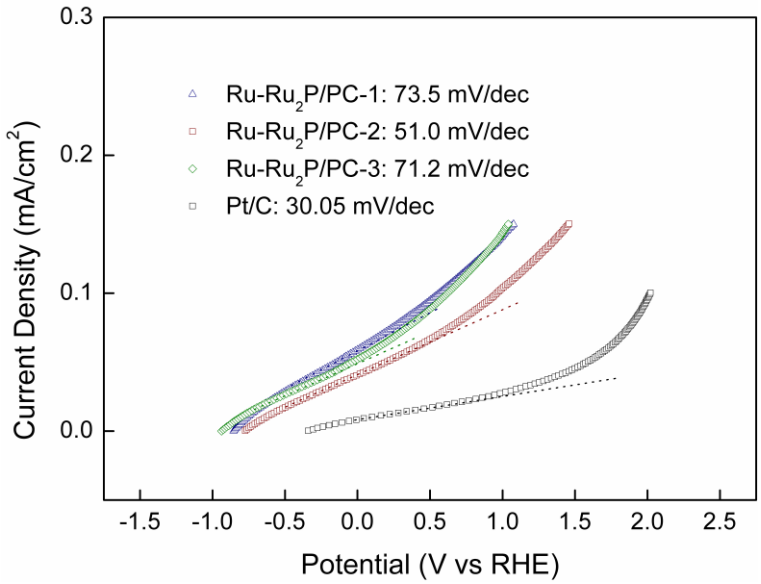


Figure S16. Tafel plots of the Ru-Ru_2P/PC catalysts and the commercial Pt/C catalyst in 0.5 M H_2SO_4 solution.

Table S1. Alkaline HER catalytic performances of the recent R and RuP_x based catalysts.

Catalyst	Overpotential at 10 mA/cm^2 in 1MKOH (mV)	Tafel slope (mV/dec)	References
Ru-Ru_2P@PC	**43.4**	**35.1**	**This work**
$Ru/C_3N_4/C$	79	--	[2]
RuP_2/NPC	52	69	[3]
Ru/CN	50	--	[4]
Ru_2P/PNC@CC	50	52	[5]
Ru_2P	54	29	[6]

References

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