Electronic Supplementary Information

Controllable fabrication of uniform ruthenium phosphide nanocrystals for hydrogen evolution reaction

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Experimental Section

Preparation of NG

For the preparation of graphene oxide (GO), graphite flakes (1.0 g) and $KMnO_4$ (6.0 g) were added into a mixture of 120 mL concentrated H_2SO_4 and 13.3 mL H_3PO_4, producing a slight exotherm to 35 ℃. The mixture was then heated to 50 ℃ and kept there under stirring for 12 h. The reaction was cooled to room temperature and poured into ice water (150 mL) with 30% H_2O_2 (10 mL). The mixture was sifted through a polyester fiber. The filtrate was centrifuged (4000 rpm for 4 h), and the supernatant was decanted away. The remaining solid material was then washed in succession with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol. The eventual solution was centrifuged (4000 rpm for 4 h) and the supernatant was decanted away. The solid was vacuum-dried overnight at room temperature, resulting 1.8 g GO. For the fabrication of NG, 150 mg GO was dispersed in 15 mL water to form a concentrated GO suspension, which was mixed with 1 mL formaldehyde solution (37 wt.%) and 0.35 g melamine. The mixture was then transferred into an autoclave and hydrothermally treated at 180 ℃ for 12 h. The obtained composite hydrogel was dried at 80 ℃ for 24 h in an oven. The dry aerogel was subsequently calcined at 750 ℃ for 5 h in N_2 atmosphere, resulting in the t final NG product.

Preparation of ruthenium phosphide (Ru_2P and RuP) on NPG

20 mg NG was firstly dispersed in 1.0 mL N,N-dimethyl formaldehyde (DMF). 30 mg TPP-Ru and the necessary PA solution (50 wt.% in water) was added and dissolved in the above dispersion. For the fabrication of Ru_2P and RuP, 0.075 mL and 1.25 mL PA solution were required respectively. The mixture was placed in an open Teflon vessel and dried at 60 ℃ slowly. After annealing at 700 ℃ for 3h, the resulting Ru_2P and RuP on NPG were obtained.

Preparation of RuNC

20 mg graphene was dispersed in 10 mL phosphate buffer solution (pH 8.5) followed by addition of 2.6 mL $RuCl_3 \cdot 3H_2O$ water solution (4 mg mL^{-1}), 40 mg dopamine hydrochloride, and 300 mg cetyl trimethyl ammonium bromide (CTAB). The mixture was treated at 140 ℃ for 6 hours. Afterwards, it was centrifuged at 3000 rpm. The obtained solid was washed by water and ethanol, subsequently dried and annealed at various temperatures for 3 hours under Ar atmosphere.

Determination of Ru loading

The determination of Ru on NPG is employed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. Briefly, the ruthenium phosphide/NPG composites were first digested in concentrated aqua regia (mixture of 6.6 M HCl and 2.1 M HNO3) at 60 ℃ overnight. The digestion solution was then pipetted and diluted to obtain a working solution. The weight loadings of Ru were averaged from twice measurements.

Electrochemical measurements

The electrochemical measurements were conducted on an electrochemical cell with conventional three-electrode system. The commercial glass carbon electrode (GCE) with the diameter of 5 mm was used as the working electrode. The current densities were normalized by the geometric surface area of the GCE. The graphite rod electrode and the saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. The working electrodes were fabricated by the following procedure: the suspensions of the as-prepared materials were drop coated onto a glassy carbon disk with the diameter of 3 mm (mass-loading ~0.06 mgRu cm^{-2}) and dried at room temperature in air for 6 h. Then 5 μL Nafion solution (0.02 wt.%) were cast on the electrode surface to adhere the materials on electrodes. The potential versus saturated calomel electrode were converted into the potential versus reversible hydrogen electrode (RHE) according $E_{\text{vs RHE}} = E_{\text{vs SCE}} + E^{\theta}_{\text{SCE}} + 0.059\ \text{pH}$.

The calibration test was conducted in a 0.25 M H_2SO_4 solution containing 10 mM $CuSO_4$ with saturated N_2 during the whole test. The electrode was first cycled between 0.23 and 0.7 V in 0.25 M H_2SO_4 with scan speed of 10mV s^{-1} for many scans as the background. Then the solution was changed into 0.25 M H_2SO_4 and 10 mM $CuSO_4$ with scan speed of 10mV s^{-1}. And the ECSA was calculated after 20 times CV scan. The ECSA was calculated by the following formula:

$$ECSA_{(cm^2\,\text{meta l}/\,g\ \text{metal})} = \frac{Q_{Cu}}{M_{\text{metal}} \times 420\mu C\ cm^{-2}}$$

The M_{metal} is the numerous loading of Ru nanoparticles on the working electrode. And Q_{Cu} is the average charge calculated from area under the voltragram of the Cu-upd CV curve.

Afterwards, the HER turnover frequency (TOF) is defined as:

$$TOF = \frac{\text{total hydrogen turnovers}/cm^{-2}\ \text{geo}}{\text{total active sites}\ /\ cm^{-2}\ \text{geo}}$$

The upper hydrogen turnovers per geometric electrode area can be calculated by the hydrogen evolution current density under a certain overpotential:

$$H_2 = \left(j\,\frac{mA}{cm^2_{geo}} \right) \times \left(\frac{1C/s}{1000mA} \right) \times \left(\frac{1mol\ e^-}{96485C} \right) \times \left(\frac{1mol\ H_2}{2mol\ e^-} \right) \times 6.02 \times 10^{23} = j \times 3.12 \times 10^{15}\, H_2/s/cm^2_{geo}$$

The total active sites per geometric electrode area can be calculated through the pre-calculated ECSA above.

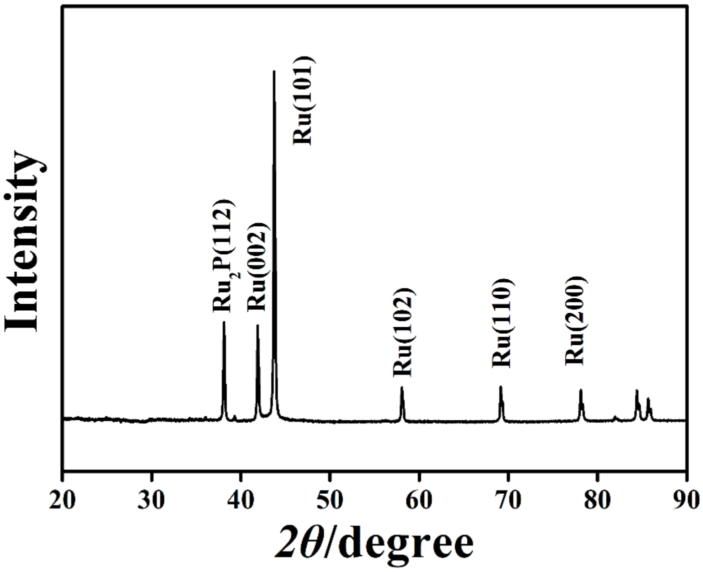

Fig. S1 XRD pattern of the ruthenium phosphide using TPP-Ru as the Ru and P precursors

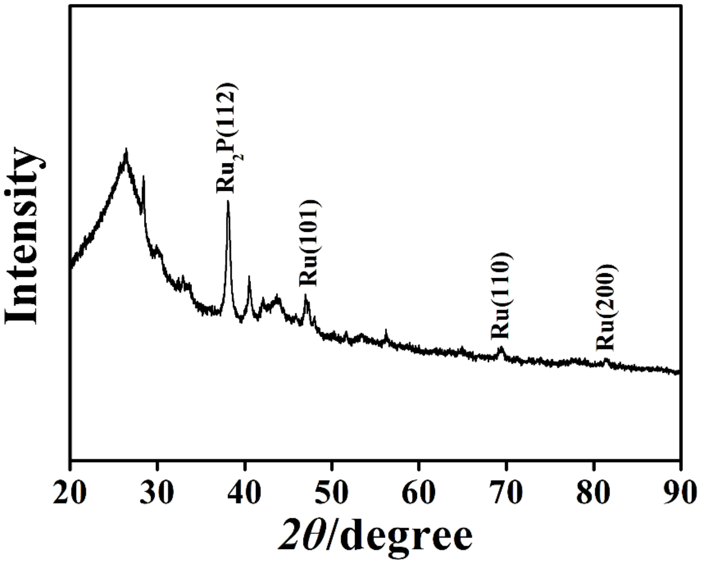

Fig. S2 XRD pattern of the ruthenium phosphide using $RuCl_3$ and PA as the Ru and P precursors, respectively

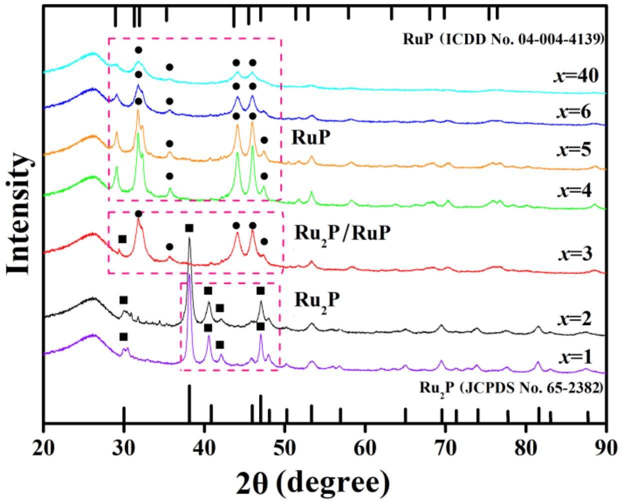

Fig. S3 XRD patterns of the obtained ruthenium phosphides as the molar ration of PA to TPP-Ru varied from 1 to 40 without NG.

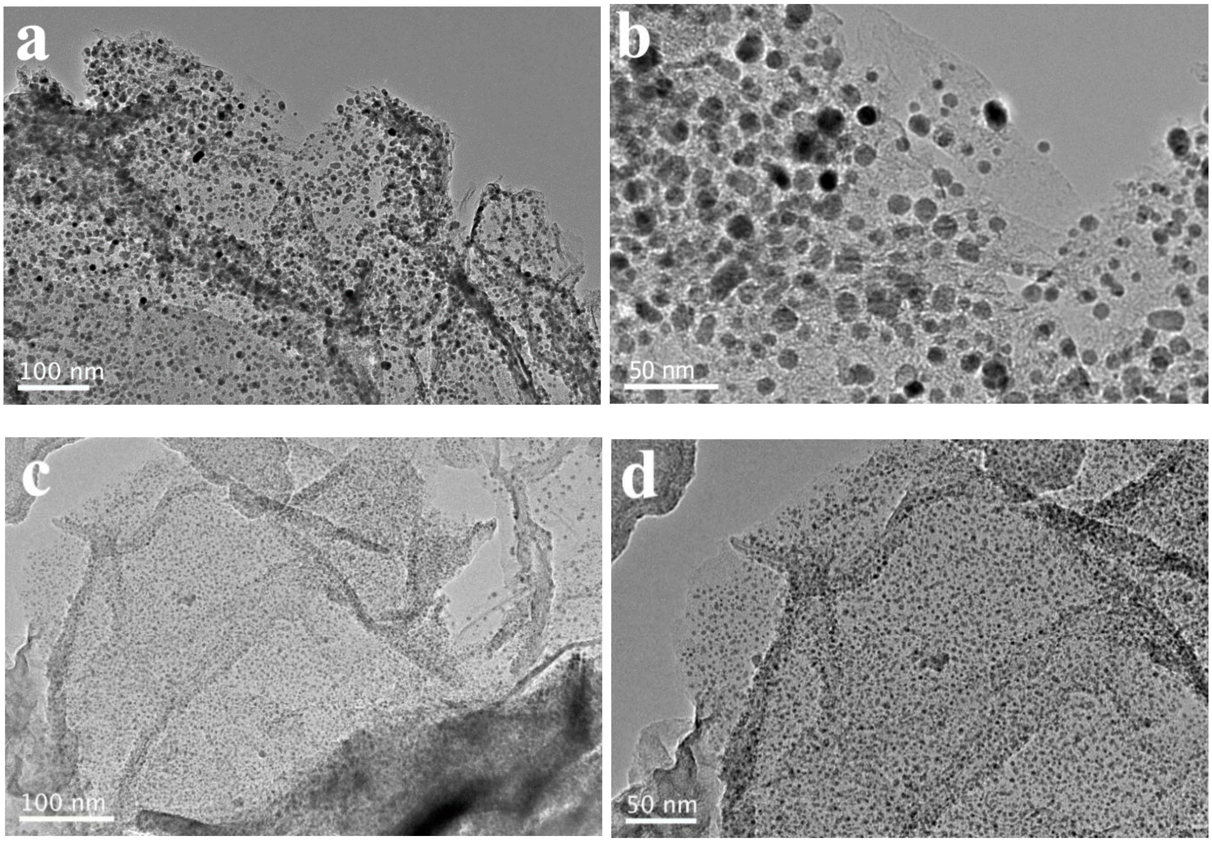

Fig. S4 TEM images of Ru_2P (a, b) and RuP (c, d) observed under the low-resolution.

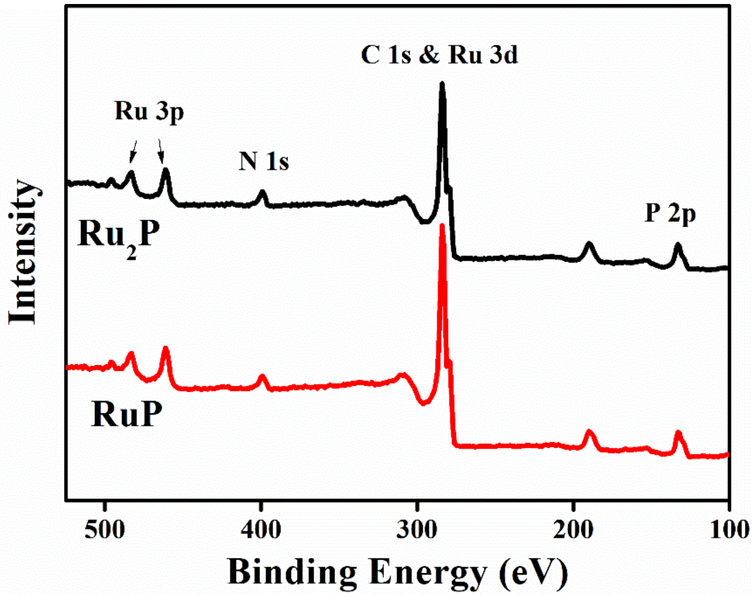

Fig. S5 XPS survey of Ru_2P and RuP supported on NG

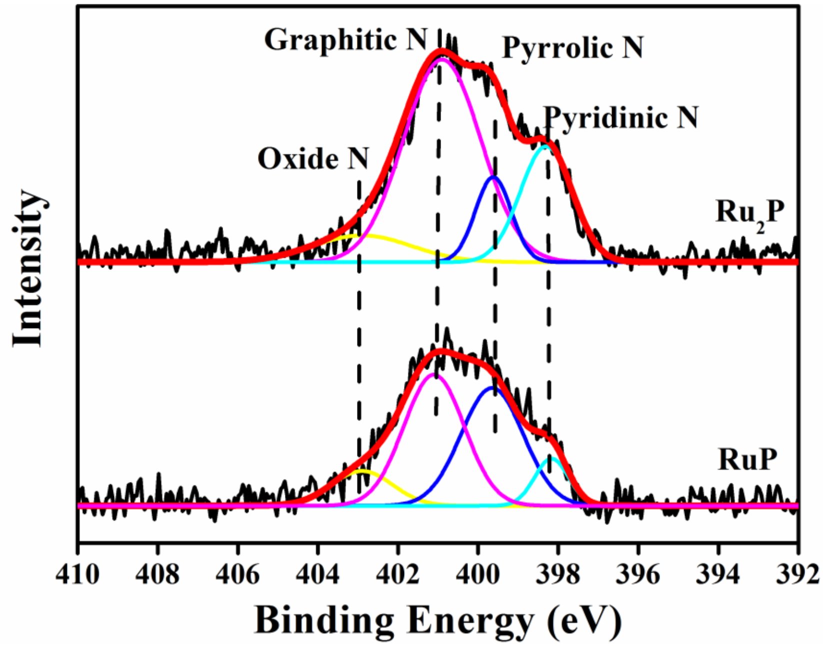

Fig. S6 N1s XPS of Ru_2P and RuP on NPG.

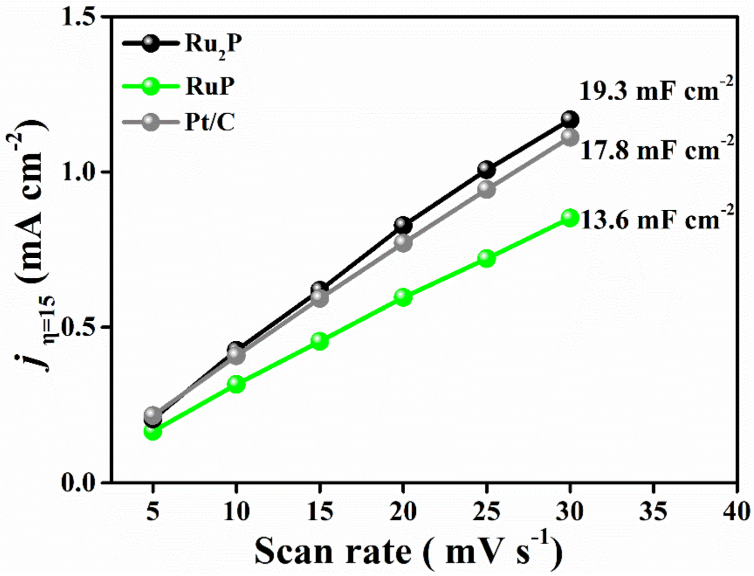

Fig. S7 The ECSA of the catalysts estimated by a double layer capacitance **(C_{dl})** measurement

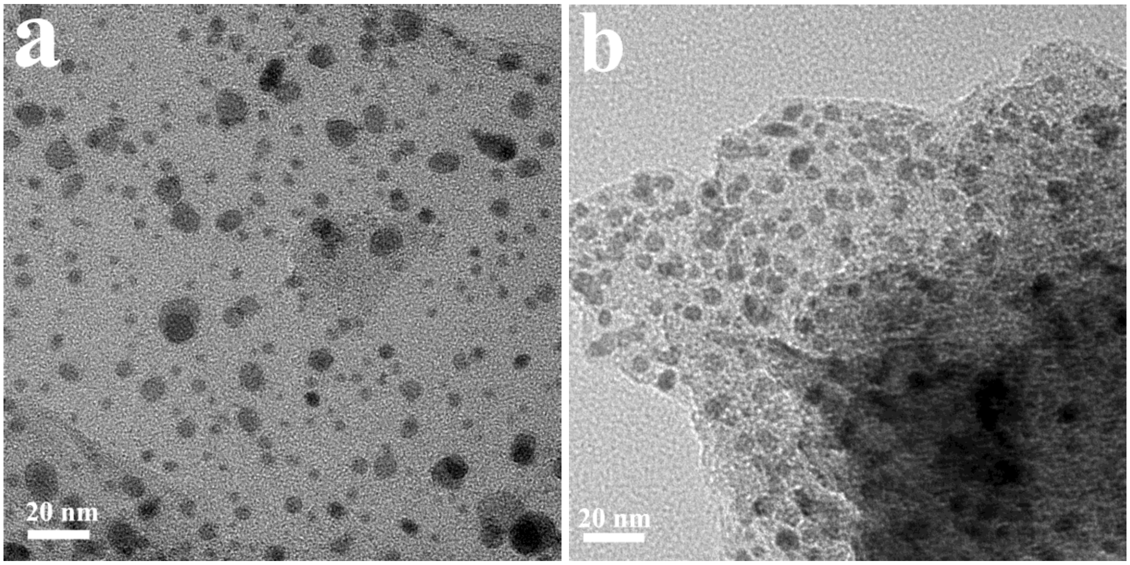

Fig. S8 TEM images of Ru_2P and RuP after 20,000 cycles.

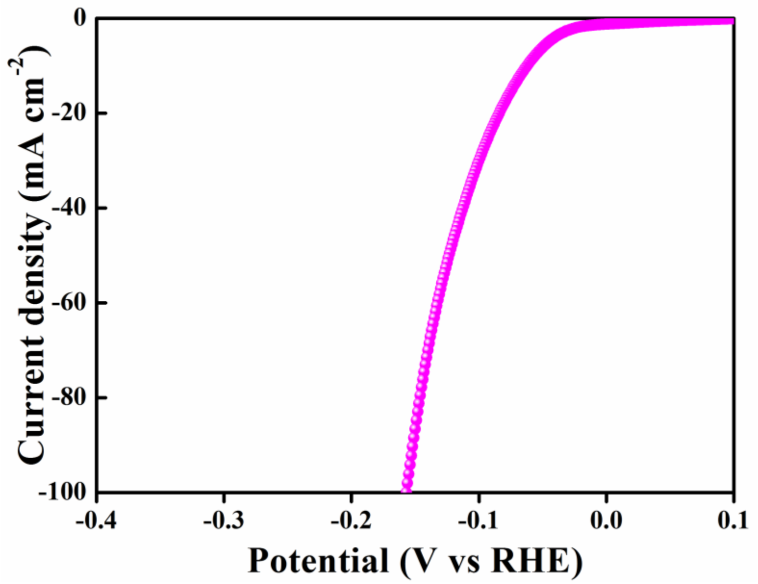

Fig. S9 The LSV curve of Ru_2P/RuP in alkaline medium (1.0 M KOH).

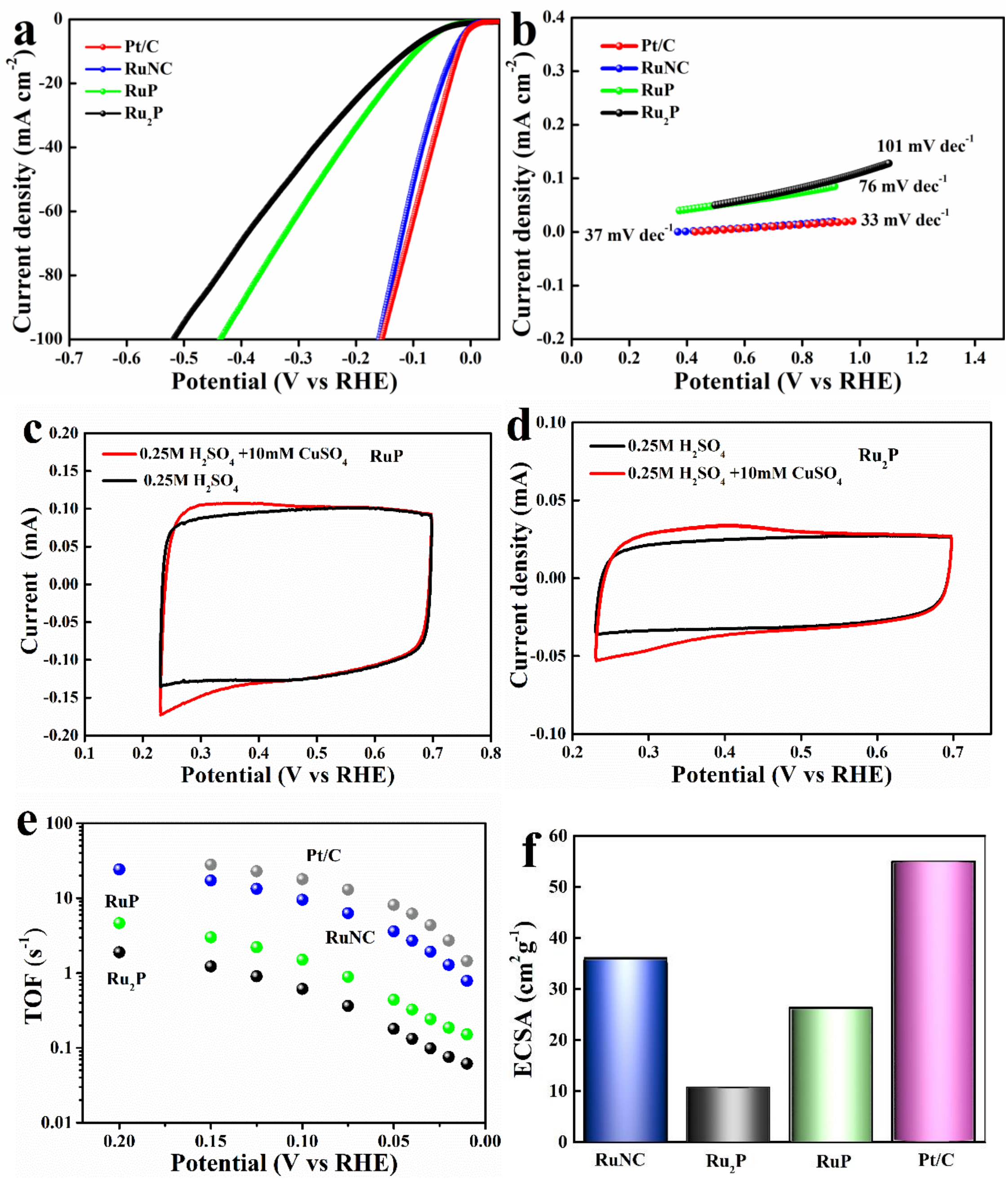

Fig. S10 The electrocatalytic performance of Ru_2P and RuP for HER in acid medium (0.5 M H_2SO_4) (a), LSV; (b) Tafel curves; (c, d) CV in H_2SO_4 (0.25 M H_2SO_4) or the mixture of H_2SO_4 (0.25 M H_2SO_4) and $CuSO_4$ (10 mM $CuSO_4$) (Cu-upd method); (e) TOF; (f) the ECSA calculated by Cu-upd method.

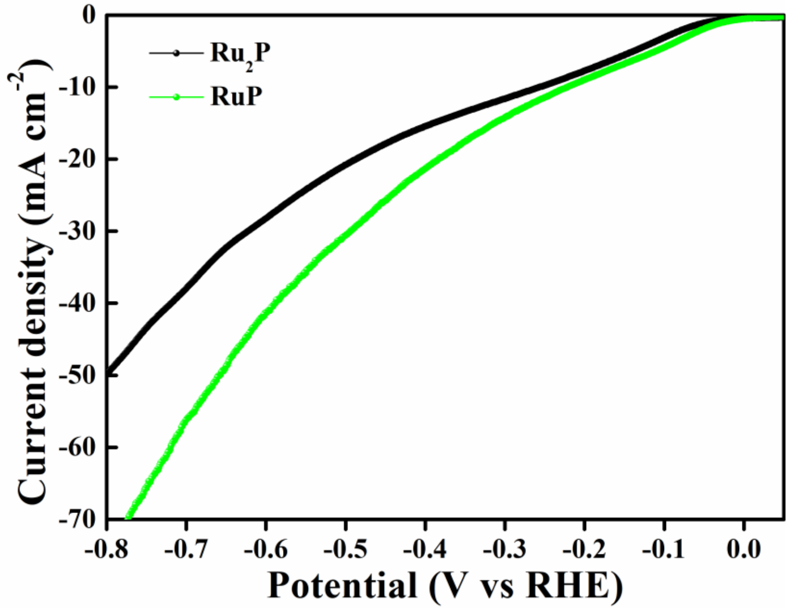

Fig. S11 LSV curves of Ru_2P and RuP in a neutral medium (1.0 M PBS)