Supporting Information

Ru Prussian blue analogue-derived Ru nanoparticles composited with a trace amount of Pt as an efficacious electrocatalyst for hydrogen evolution reaction

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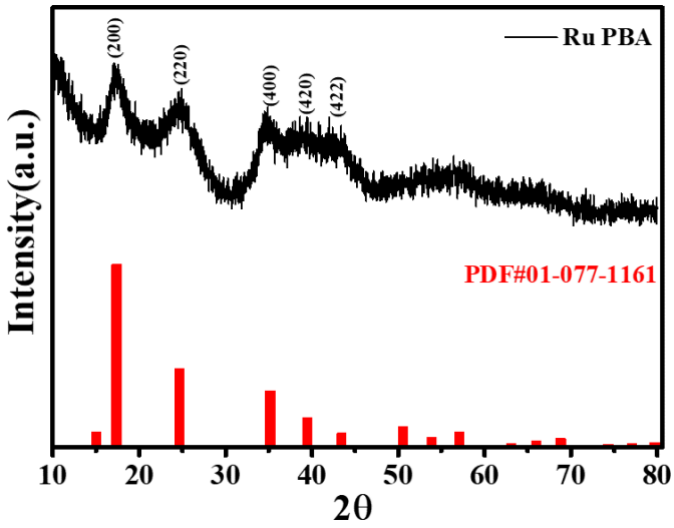

Fig. S1 Powder X-ray diffraction of Ru-PBA.

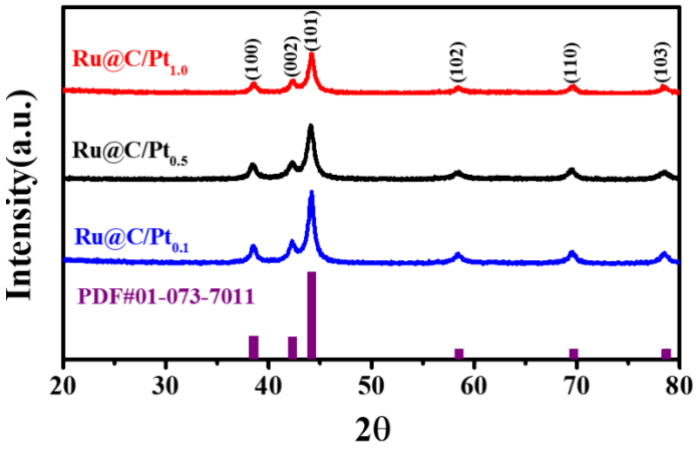

Fig. S2 PXRD pattern of Ru@C/$Pt_{0.1}$, Ru@C/$Pt_{0.5}$, and Ru@C/$Pt_{1.0}$.

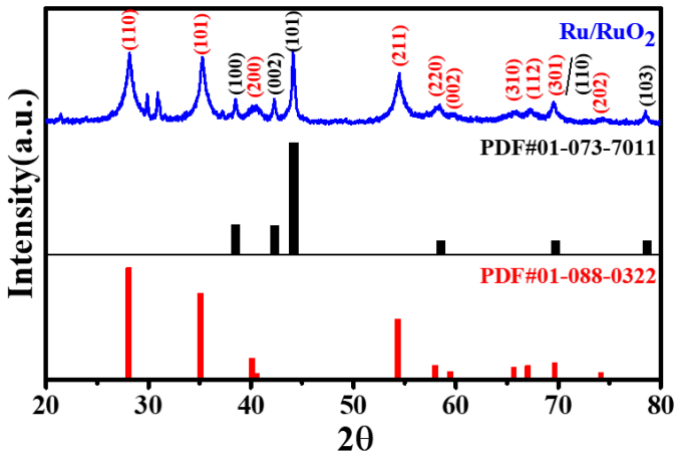

Fig. S3 Powder X-ray diffraction for Ru-PBA annealed in free air.

The performance of Ru@C/$Pt_{0.5}$ has been checked in different electrolytes such as 0.5 M KOH (pH=13.69), 0.5 M HCl (pH=0.3) and 0.5 M Na_2SO_4 (pH=7.2). The sample casted glassy carbon rotating disk electrode (GCRDE), bare graphite rod, and aqueous Ag/AgCl were taken as working, counter, and reference electrodes respectively for the electrolytes 0.5 M H_2SO_4, 0.5 M HCl and 0.5 M Na_2SO_4. The linear sweep voltammograms were obtained at 5 mV/s and 2000 rpm in all the electrolytes. The LSV in 0.5 M NaOH was carried out by using Hg/HgO, glassy carbon rotating disk electrode (GCRDE), and bare graphite rod as reference, working and counter electrode respectively. All the potentials were converted into RHE by using the following Nernst equation:

For Ag/AgCl:

$$E_{RHE} = E_{\frac{Ag}{AgCl}} + 0.059pH + E^0_{\frac{Ag}{AgCl}}$$

For Hg/HgO:

$$E_{RHE} = E_{\frac{Hg}{HgO}} + 0.059pH + E^0_{\frac{Hg}{HgO}}$$

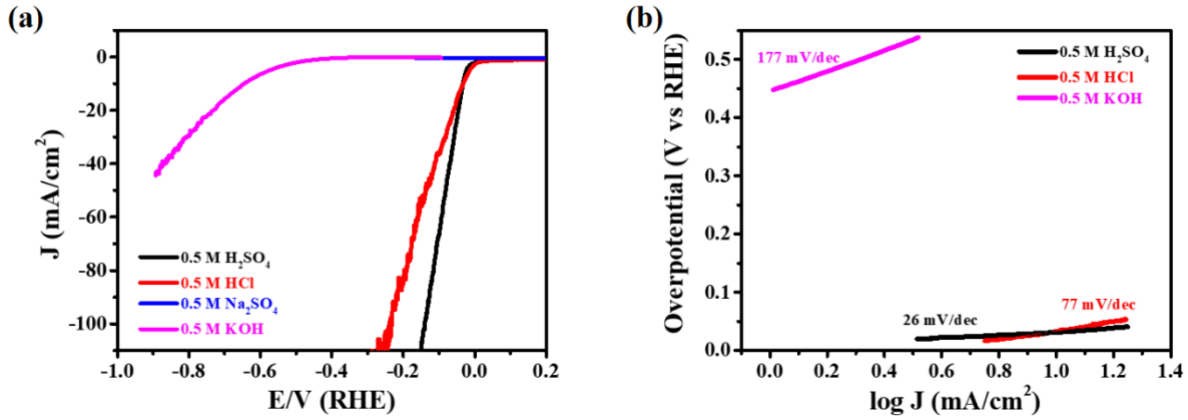

Fig. S4 (a) Linear sweep voltammograms, (b) Tafel slopes for Ru@C/$Pt_{0.5}$ in 0.5 M H_2SO_4, 0.5 M HCl, 0.5 M Na_2SO_4 and 0.5 M KOH.

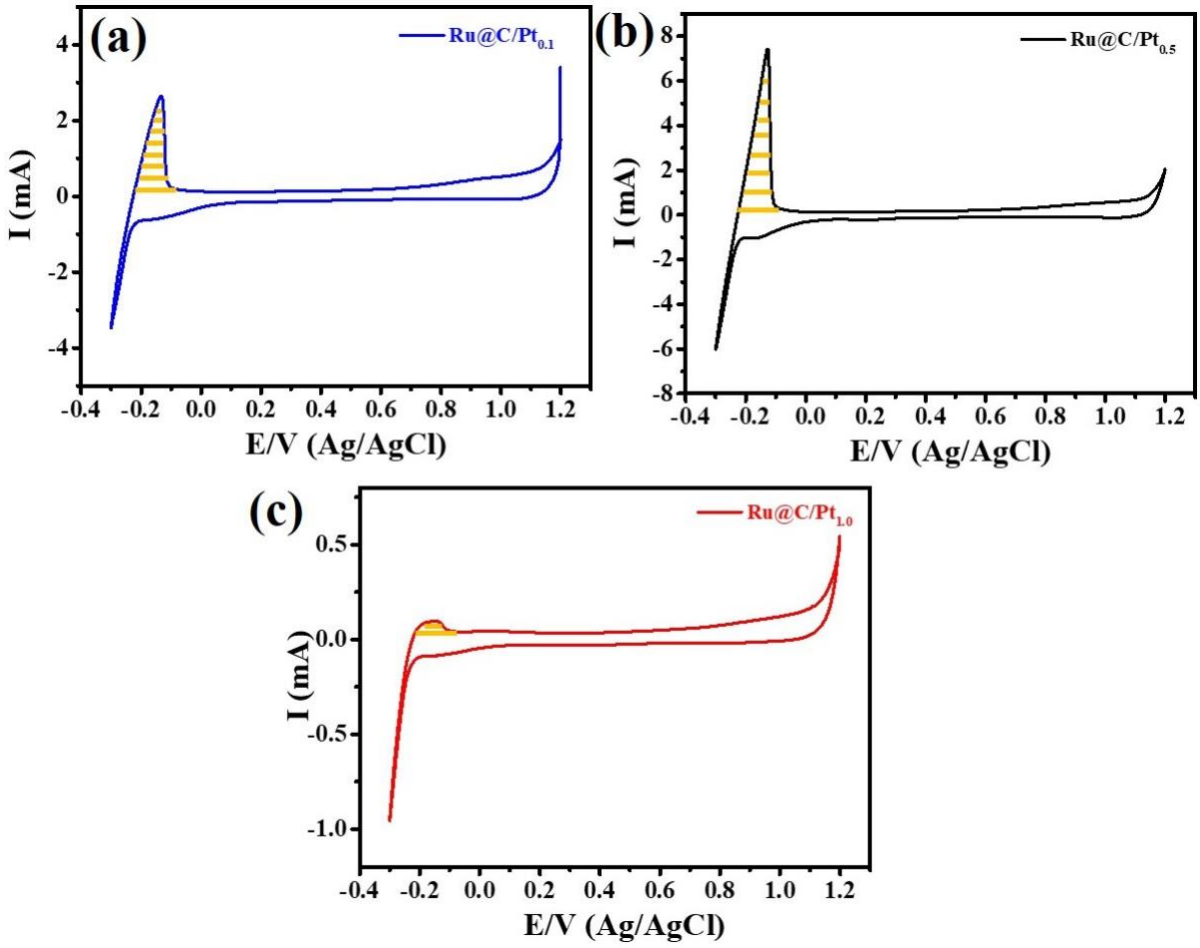

Fig. S5 Cyclic Voltametric profile of Ru@C/$Pt_{0.1}$, Ru@C/$Pt_{0.5}$ and Ru@C/$Pt_{1.0}$ electrode in 0.5 M H_2SO_4 at a sweep rate of 10 mV/s.

Here, the charge involved for the hydrogen adsorption (QH) is estimated from the area under the potential window associated with the oxidation curve. The electrochemically accessible surface area (ECSA) of Ru@C/$Pt_{0.1}$, Ru@C/$Pt_{0.5}$, and Ru@C/$Pt_{1.0}$ was calculated with reference to the standard value of 210 μC/cm^2.

Here, 210 μC/cm^2 is the charge required for the monolayer adsorption of hydrogen on the Pt surface.[1]

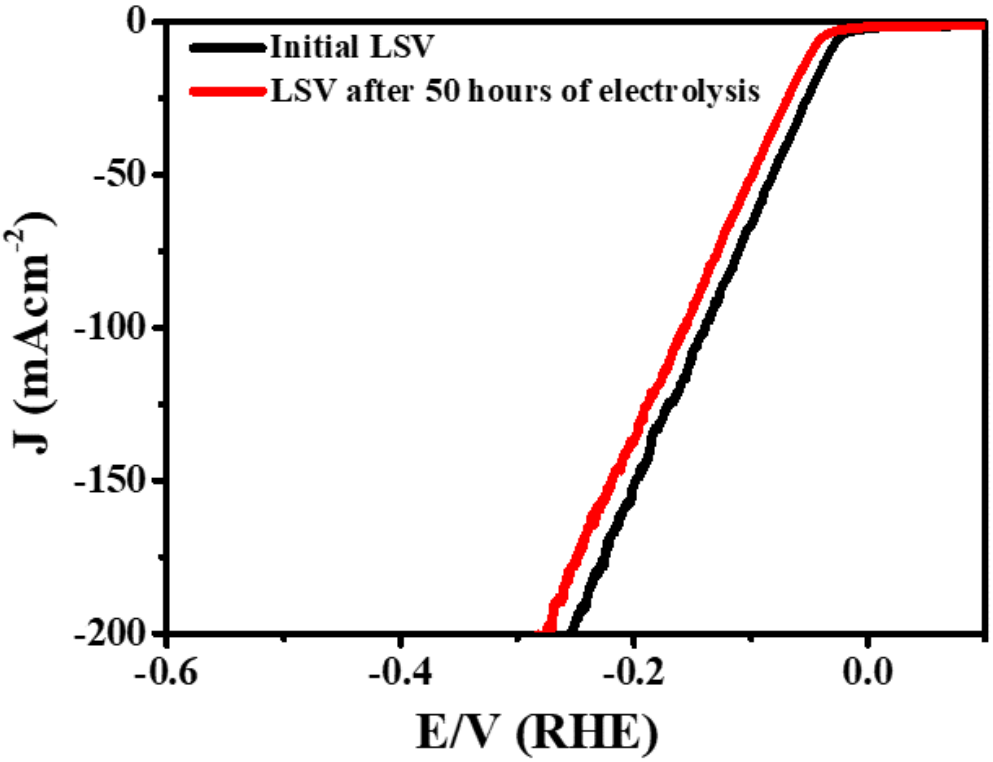

Fig. S6 Linear sweep voltammogram of initial and after 50 hours of electrolysis. The sweep rate was 5 mV/s.

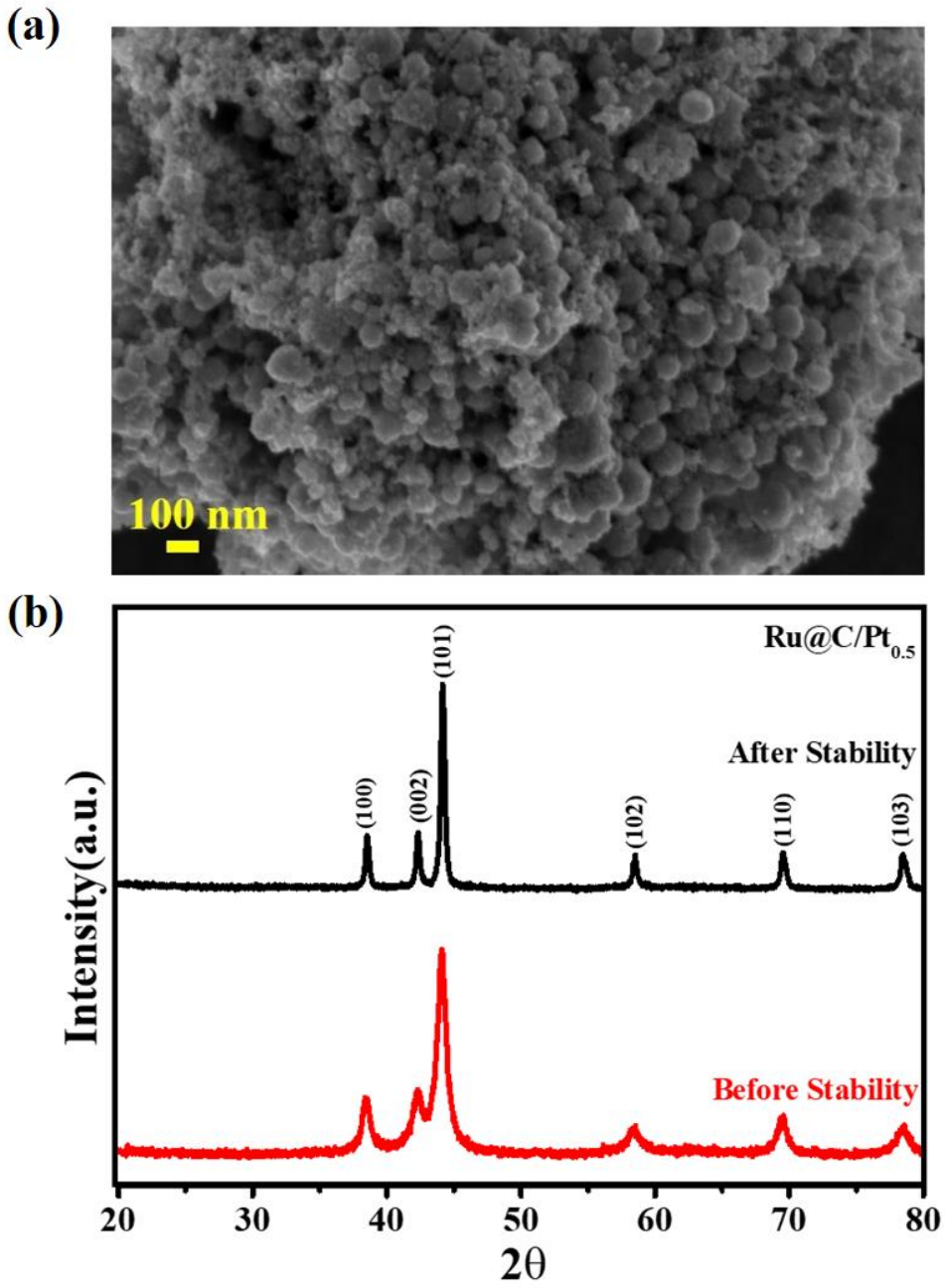

Fig. S7 (a) FESEM and (b) PXRD pattern of the Ru@C/$Pt_{0.5}$ after the stability test for 50 hours.

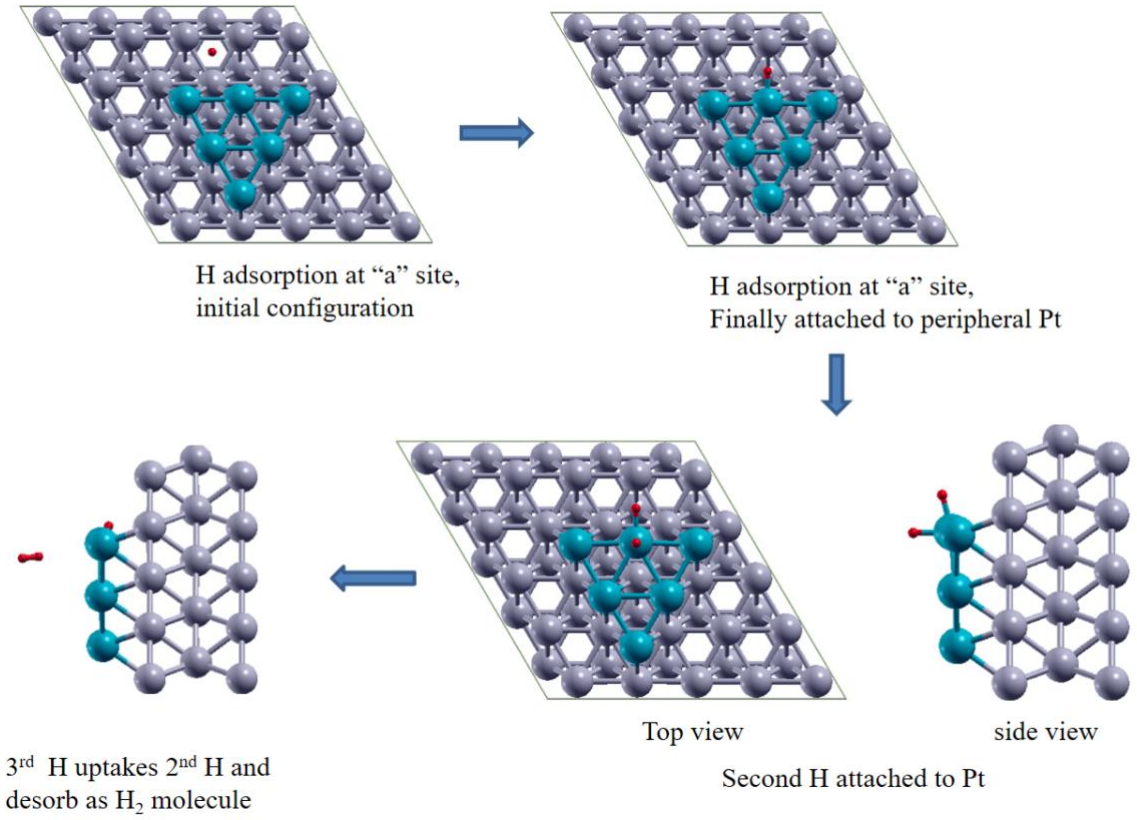

Fig. S8: Stepwise H atom adsorption and desorption process from site 'a' of $RuPt_6$ surface. (Grey, cyan and red colour represents Ru, Pt and H respectively.)

Table S1: ICP-OES analysis shows the content of Ru and Pt in Ru@C, Ru@C/$Pt_{1.0}$, Ru@C/$Pt_{0.5}$, and Ru@C/$Pt_{0.1}$

	Ru	**Pt**
Ru@C	29.11%	0%
Ru@C/$Pt_{1.0}$	42.16%	7.255%
Ru@C/$Pt_{0.5}$	49.975%	2.6%
Ru@C/$Pt_{0.1}$	37.97%	0.16%

Table S2: Gas chromatography measurement of generated H_2 during HER by using Ru@C/$Pt_{0.5}$ catalyst.

Time (min)	**H_2 concentration (ppm)**
0	0
5	1017.5
30	2431.5
Another 30 minutes	2576

Table S3: The comparison of overpotential and Tafel slope of the reported materials with the Ru@C/$Pt_{0.5}$.

	Loading density (μgcm^{-2})	**Electrolyte**	**Overpotential at 10 $mAcm^{-2}$ (mV)**	**Tafel Slope ($mVdec^{-1}$)**	**Reference**
RuP_2@NPC	1000	0.5M H_2SO_4	38	38	2
PtRu@RFCS	354	0.5M H_2SO_4	19.7	27.2	3
v-$Pt_{29}Pd_3Ru_{62}Te_6$ AS	285	0.5M H_2SO_4	39	32	4
Ni@Ni_2P–Ru HNRs	283	0.5M H_2SO_4	31	35	5
NiRu@N–C	273	0.5M H_2SO_4	50	36	6
Ru–MoO_2	285	0.5M H_2SO_4	55	44	7
Ru@Co–SAs/N–C	285	0.5M H_2SO_4	57	55	8
v-$Pt_{29}Pd_3Ru_{62}Te_6$ AS	285	1M KOH	22	22	9
Ni@Ni_2P–Ru HNRs	283	1M KOH	31	41	5
Ru_1CoP/CDs	420	1M KOH	51	73.4	9
$NiRu_2$@NC-600		0.5M H_2SO_4	85	45.54	10
$Pt_{0.3}Ru_{0.7}$NP/OMC	0.44 Pt 0.39 Ru	0.5 M H_2SO_4	42.3	37	11
Ru@C/$Pt_{0.5}$	263	0.5 M H_2SO_4	32	26	This work

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