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Supporting Information

Amorphous RuPd bimetallene for hydrogen evolution reaction in acidic and alkaline conditions: A first-principles study

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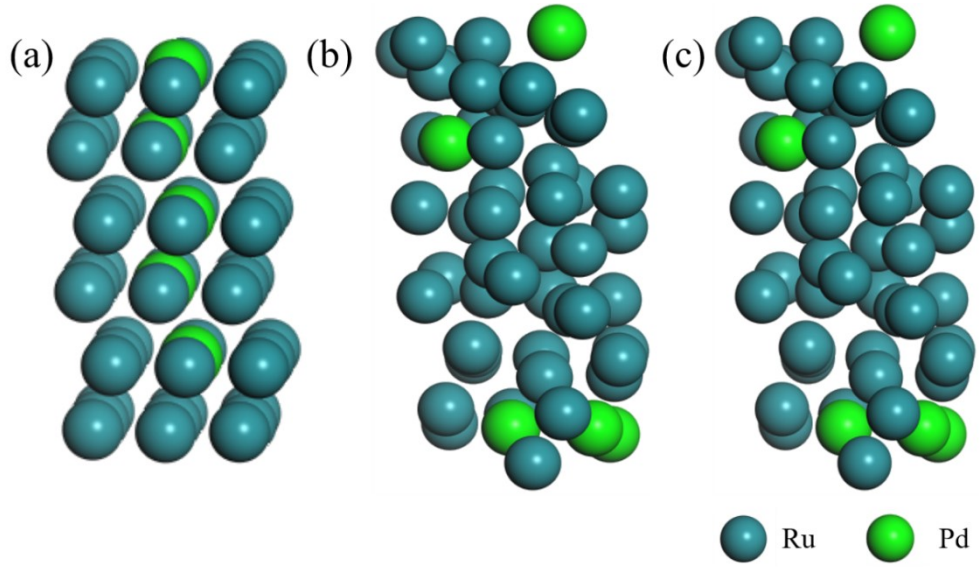

Fig. S1. (a) Original crystal structure. The obtained structure that (b) the crystal cell was relaxed for 20 ps at 2600 K, (b) then the disordered structure was relaxed to a local energy minimum at 0 K.

Change of free energy of OH*

The adsorption energy of different adsorbents (H_2O*, H-OH*, OH*, H*) in the alkaline HER process is calculated as follows,

$$\Delta E_{H_2O^*} = E_{H_2O^*} - E* - E_{H_2O} \quad \text{S1}$$

$$\Delta E_{H-OH^*} = E_{H-OH^*} - E* - E_{H_2O} \quad \text{S2}$$

$$\Delta E_{OH^*+H^*} = E_{OH^*+H^*} - E* - E_{H_2O} \quad \text{S3}$$

$$\Delta E_{OH^*} = E_{OH^*} - E* - (E_{H_2O} - 1/2E_{H_2}) \quad \text{S4}$$

$$\Delta E_{H^*} = E_{H^*} - E* - 1/2E_{H_2} \quad \text{S5}$$

According to the formula $H_2 \rightarrow 2(H^+ + e^-)$, the energy of the hydroxide can be calculated by the following formula,

$$E_{OH^-} = E_{H_2O} - 1/2E_{H_2} \quad \text{S6}$$

The change of free energy (ΔG) for each step of alkaline HER is all obtained by the following formula,

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \quad \text{S7}$$

where ΔE, ΔZPE and ΔS represent the reaction energy, zero energy difference and entropy change at each step. The detailed calculation data above are shown in Table S3, 4.

The calculation about exchange current density

Considering that part of the electrochemical cell is hydrogen evolution on the metal electrode, the current density during the hydrogen evolution process can be expressed as[1],

$$i = -er \quad \text{S8}$$

where r is the net rate. In equilibrium, the exchange current density is related to forward (or backward) rate, and can be written as follows,

$$i = -er_1. \quad \text{S9}$$

The forward rate can be written as follows,

$$r_1 = k_1(1-\theta)c_{H^+}, \quad \text{S10}$$

where k_1 is rate constant, θ is H coverage, c_{H^+} is the concentration of protons in the electrolyte. The coverage of hydrogen can be calculated as follows,

$$\theta = \frac{K}{1+K}, \quad \text{S11}$$

where $K = exp(\frac{-\Delta G_{H^*}}{kT})$. When $\Delta G_{H^*} < 0$, $k_1 = k_0$. For any PH less than 7, the exchange current density may be expressed as,

$$i_0 = -ek_0 \frac{1}{1+\exp\left(-\Delta G_{H^*}/kT\right)} 10\hat{}(-PH) \quad \text{S12}$$

When $\Delta G_{H^*} > 0$, $k_1 = k_0 exp(-\Delta G_{H^*}/kT)$. In this case, the exchange current density can be expressed as:

$$i_0 = -ek_0 \frac{1}{1+\exp\left(-\Delta G_{H^*}/kT\right)} \exp\left(-\Delta G_{H^*}/kT\right) 10\hat{}(-PH) \quad \text{S13}$$

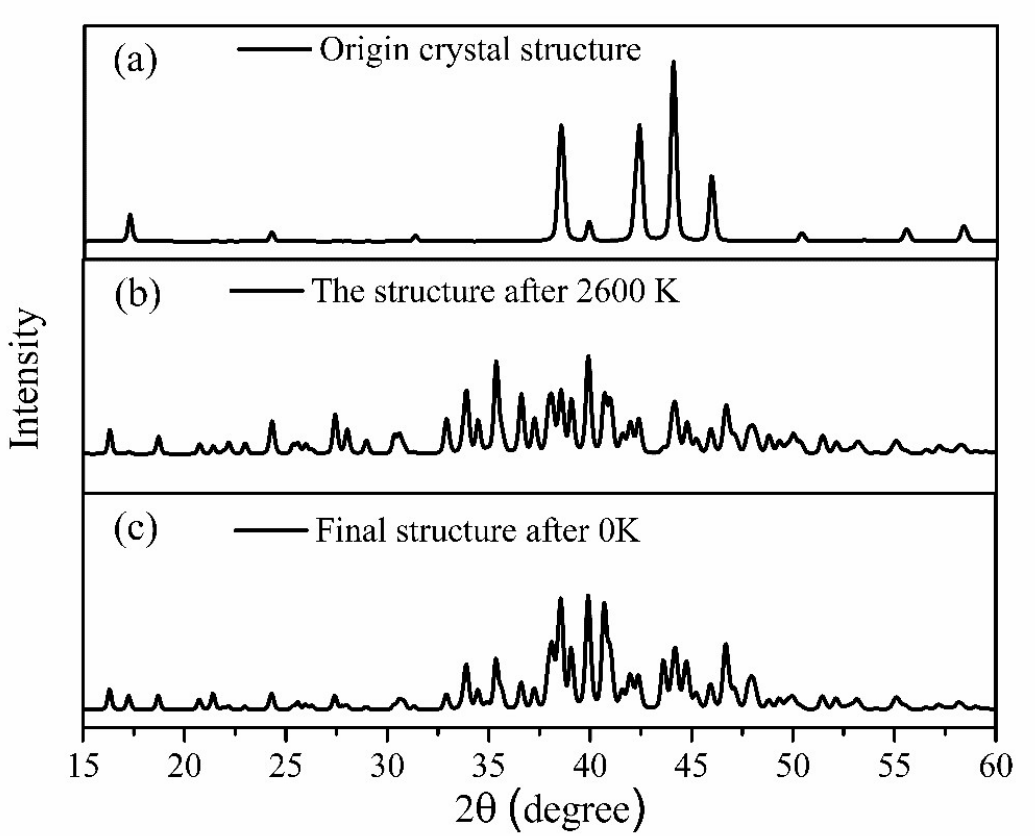

Fig.S2. X-ray diffraction pattern for (a) original crystal structure, (b) the obtained structure after 2600 K, (b) final structure after 0 K, which correspond to Fig. S1.

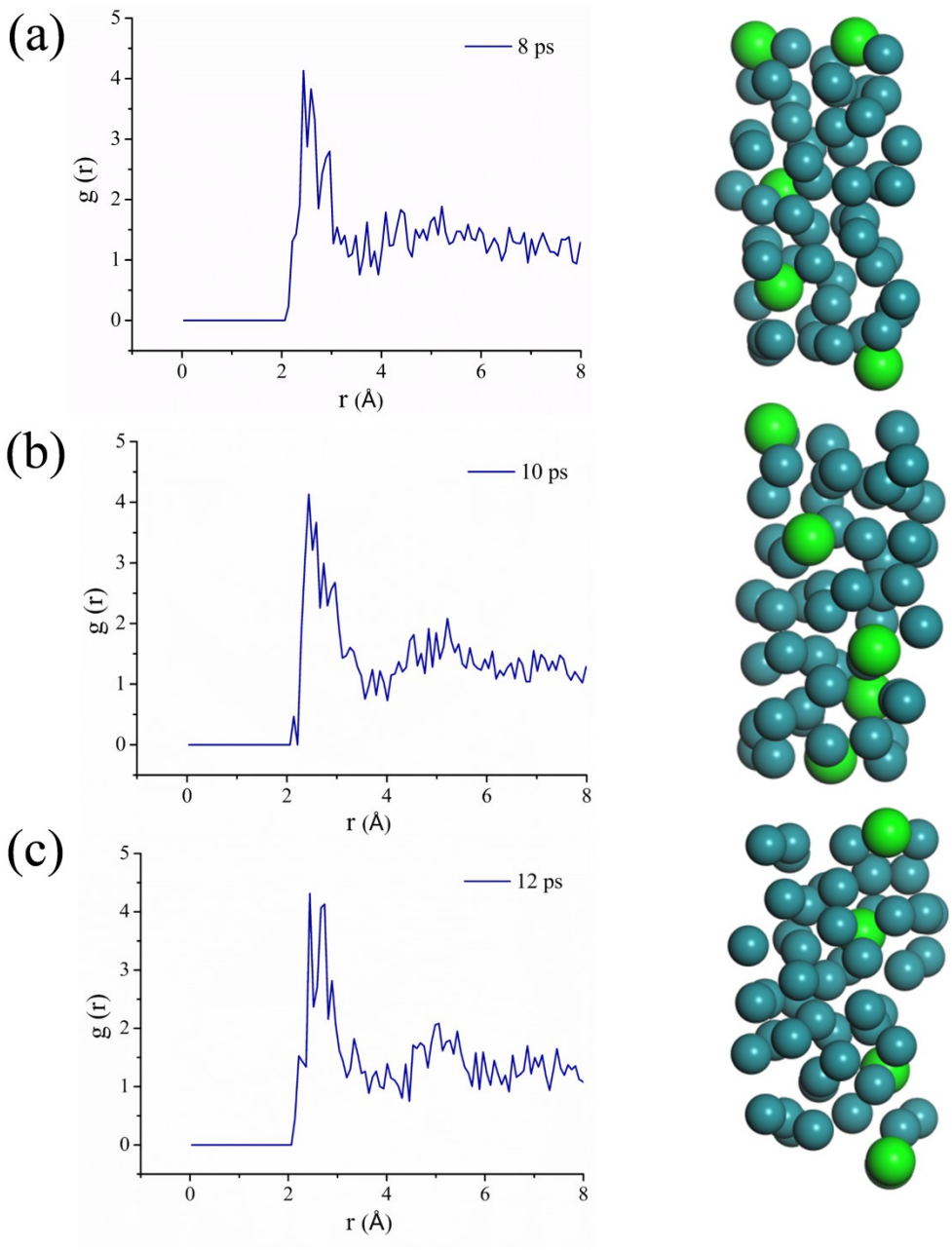

Fig.S3. The radial distribution functions and snapshots of structure of c-RuPd at (a) 8 ps, (b)10 ps and (c)12 ps in the process of annealing under 2600 K.

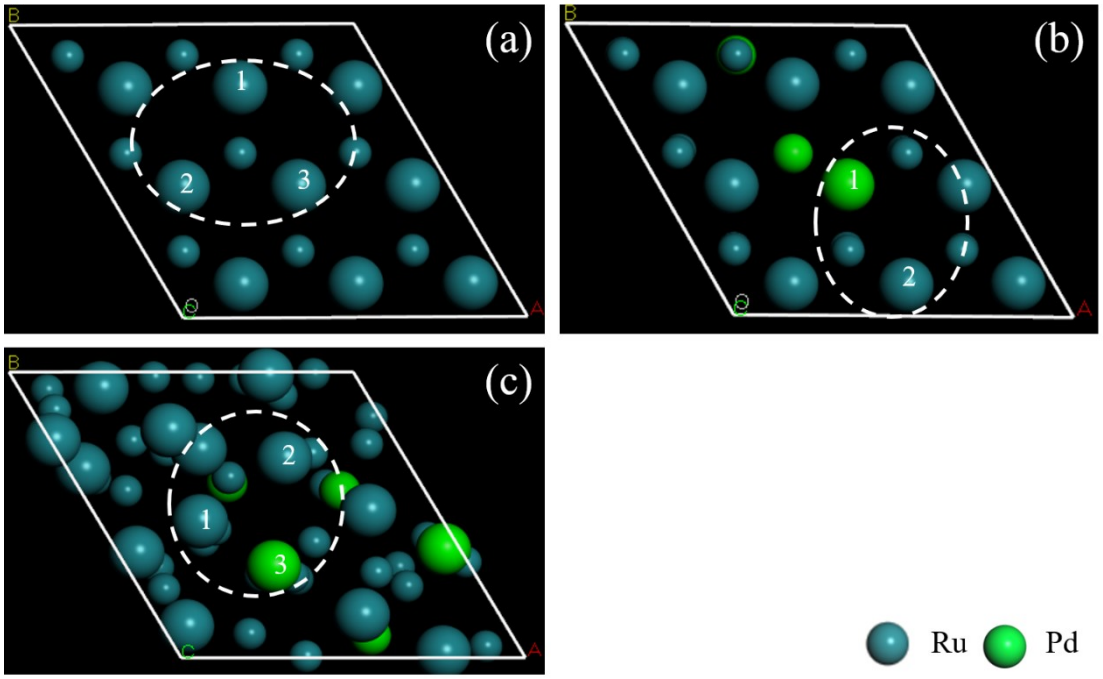

Fig. S4. The atoms at the optimal H adsorption site (numbered in the circle) on (a) Ru (0001), (b) c-RuPd, and (c) am-RuPd, which were selected for the partial density of states (PDOS) in Fig. 4a.

Table S1. ΔG_H*and $Logi_0$ values at different site for Ru (0001), c-RuPd and am-RuPd

site	ΔG_H*(eV)	$Logi_0$ (A/site)
Pt (111)	-0.140	-18.848
Ru (0001)	-0.272	-21.067
c-RuPd-1	-0.308	-21.664
c-RuPd-2	-0.305	-21.624
c-RuPd-3	-0.164	-19.252
c-RuPd-4	-0.143	-18.906
c-RuPd-5	-0.268	-21.000
c-RuPd-6	-0.211	-20.036
am-RuPd-1	-0.225	-20.279
am-RuPd-2	-0.224	-20.266
am-RuPd-3	-0.041	-17.249
am-RuPd-4	-0.043	-17.289
am-RuPd-5	0.108	-18.319
am-RuPd-6	-0.138	-18.820

Table S2 Zero energy difference (ΔE_{ZPE}) and entropy change ($T\Delta S$) under different temperature for H*

	TΔS					ΔE_{ZPE}
	300K	320 K	340K	360K	380K	
H* (Pt)	-0.21	-0.22	-0.23	-0.24	-0.26	0.1
H* (Ru(0001))	-0.21	-0.23	-0.24	-0.25	-0.27	0.02
H*(c-RuPd)	-0.21	-0.23	-0.24	-0.26	-0.27	0.02
H*(am-RuPd)	-0.2	-0.21	-0.22	-0.23	-0.25	0.02

Table S3. ΔG_H*and $Logi_0$ values at different site for Ru (0001), c-RuPd and am-RuPd at 300K-380K

	ΔG_H*(eV)				
site	300K	320 K	340 K	360 K	380K
Pt (111)	-0.14	-0.13	-0.12	-0.11	-0.09
Ru (0001)	-0.272	-0.252	-0.242	-0.232	-0.212
c-RuPd-1	-0.308	-0.288	-0.278	-0.258	-0.248
c-RuPd-2	-0.305	-0.285	-0.275	-0.255	-0.245
c-RuPd-3	-0.164	-0.144	-0.134	-0.114	-0.104
c-RuPd-4	-0.143	-0.123	-0.113	-0.093	-0.083
c-RuPd-5	-0.268	-0.248	-0.238	-0.218	-0.208
c-RuPd-6	-0.211	-0.191	-0.181	-0.161	-0.151
am-RuPd-1	-0.225	-0.195	-0.185	-0.165	-0.155
am-RuPd-2	-0.224	-0.194	-0.184	-0.164	-0.154
am-RuPd-3	-0.041	-0.011	0.001	0.021	0.031
am-RuPd-4	-0.043	-0.013	-0.003	0.023	0.033
am-RuPd-5	0.108	0.138	0.148	0.168	0.178
am-RuPd-6	-0.138	-0.108	-0.098	-0.078	-0.068

Table S4. H_2O adsorption energy (ΔE_{H2O}*) and H_2O adsorption free energy (ΔG_{H2O}*) for different H_2O adsorption configuration

model	ΔE_{H2O}*	ΔG_{H2O}*
Ru	-0.387	0.110
c-RuPd-m1	-0.436	0.124
c-RuPd-m1	-0.169	0.391
am-RuPd-m1	-0.638	-0.101
am-RuPd-m2	-0.448	0.089
am-RuPd-m3	-0.572	-0.035
am-RuPd-m4	-0.493	0.044
am-RuPd-m5	-0.213	0.324
am-RuPd-m6	-0.216	0.321
am-RuPd-m7	-0.120	0.417

Table S5. Adsorption Energies (ΔE), zero energy difference (ΔE_{ZPE}), the product of temperature and entropy change ($T\Delta S$) and free energy (ΔG) for different intermediate on H_2O dissociation

	intermediate	ΔE	ΔE_{ZPE}	$T\Delta S$	ΔE_{ZPE}-$T\Delta S$	ΔG
Ru (0001)	H_2O*	-0.387	0.066	-0.431	0.497	0.11
	H-OH*	0.445	-0.133	-0.50	0.367	0.812
	OH*+H*	-0.455	-0.048	-0.525	0.477	0.022
c-RuPd	H_2O*	-0.436	0.072	-0.488	0.56	0.124
	H-OH*	0.378	-0.124	-0.505	0.381	0.759
	OH*+H*	-0.277	-0.079	-0.521	0.442	0.165
am-RuPd	H_2O*	-0.572	0.076	-0.461	0.537	-0.035
	H-OH*	-0.080	-0.099	-0.519	0.42	0.34
	OH*+H*	-1.239	-0.071	-0.489	0.418	-0.821

Table S6. The entropy change (TΔS) for different intermediate on H_2O dissociation at 320-380K.

□ □	intermediate	ΔE_{ZPE}	TΔS			
			320K	340K	360K	380K
Ru (0001)	H2O*	0.066	-0.458	-0.4844	-0.511	-0.537
	H-OH*	-0.133	-0.533	-0.564	-0.597	-0.628
	OH*+H*	-0.048	-0.559	-0.564	-0.597	-0.628
c-RuPd	H2O*	0.072	-0.521	-0.553	-0.585	-0.616
	H-OH*	-0.124	-0.538	-0.57	-0.603	-0.634
	OH*+H*	-0.079	-0.557	-0.591	-0.626	-0.659
am-RuPd	H2O*	0.076	-0.49	-0.518	-0.547	-0.575
	H-OH*	-0.099	-0.554	-0.588	-0.623	-0.656
	OH*+H*	-0.071	-0.52	-0.55	-0.58	-0.609

Table S7. The free energy (Δ*G*) for different intermediate on H_2O dissociation at 320 -380K.

□	intermediate	ΔE	ΔG			
			320K	340K	360K	380K
Ru (0001)	H2O*	-0.39	0.137	0.1634	0.19	0.216
	H-OH*	0.445	0.845	0.876	0.909	0.94
	OH*+H*	-0.46	0.056	0.061	0.094	0.125
c-RuPd	H2O*	-0.44	0.157	0.189	0.221	0.252
	H-OH*	0.378	0.792	0.824	0.857	0.888
	OH*+H*	-0.28	0.201	0.235	0.27	0.303
am-RuPd	H2O*	-0.57	-0.006	0.022	0.051	0.084
	H-OH*	-0.08	0.375	0.409	0.444	0.477
	OH*+H*	-1.24	-0.79	-0.76	-0.73	-0.7

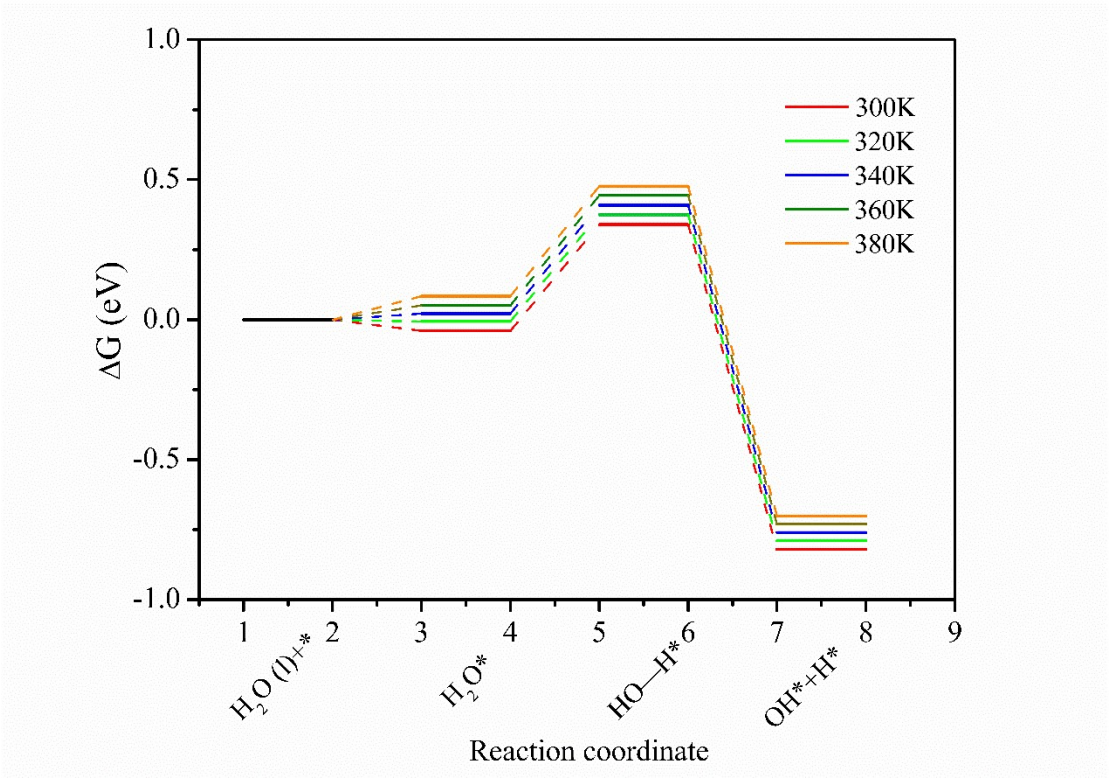

Fig. S5. The free energy diagram of H_2O dissociation processes for am-RuPd at 300-380K.

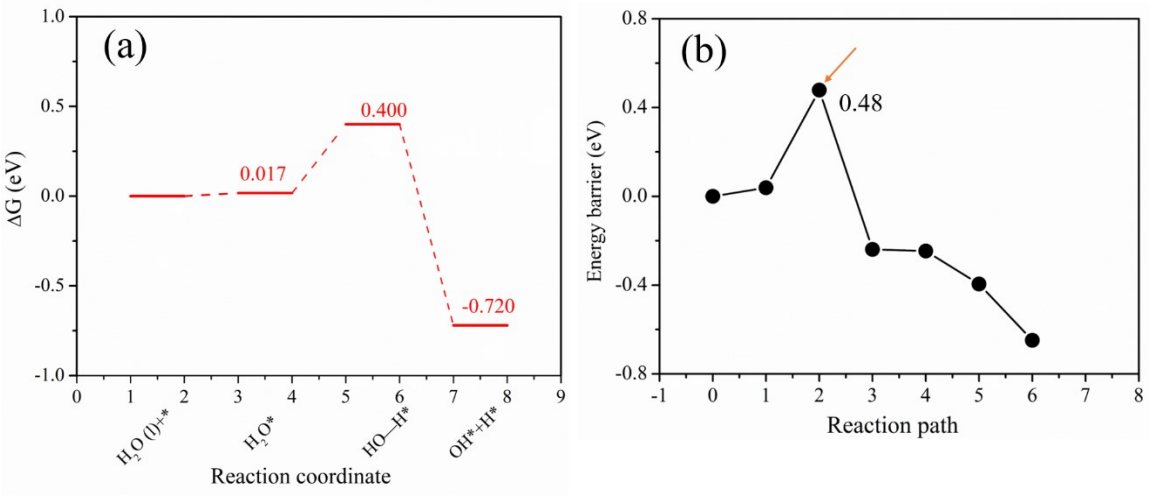

Fig. S6. (a) The free energy diagram of H_2O dissociation processes and (b) the reaction path of H_2O dissociation for am-RuPd calculated by RPBE.

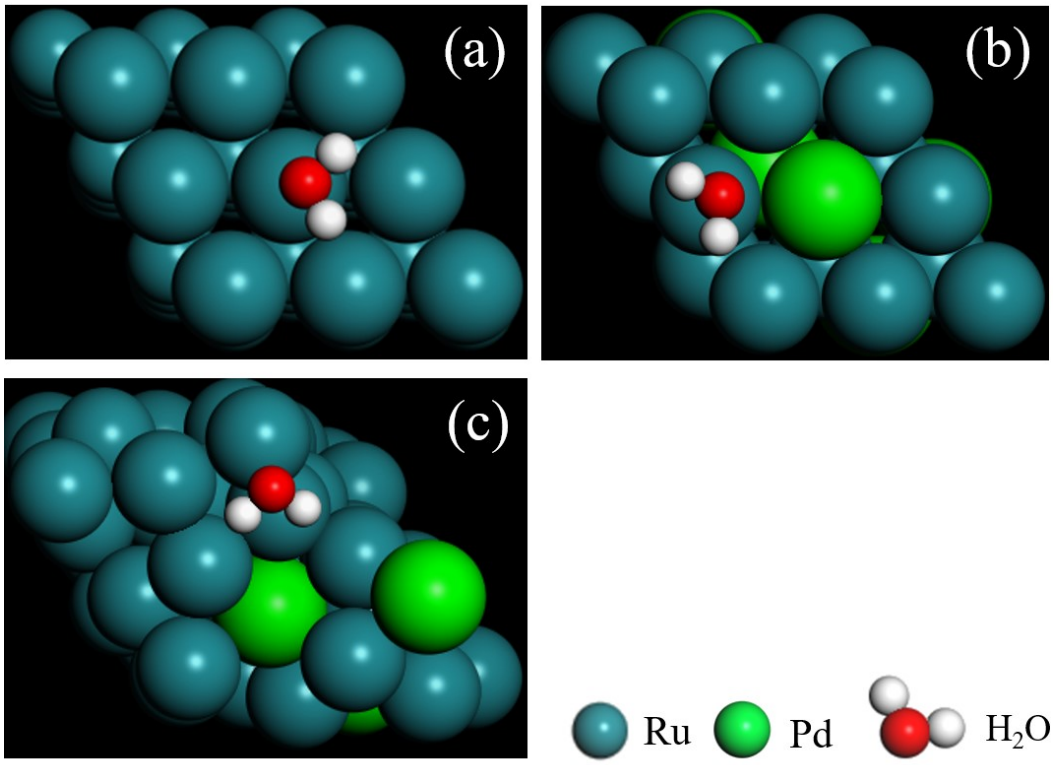

Fig. S7. H_2O adsorption structure on (a) Ru (0001), (b) c-RuPd, (c) am-RuPd corresponding to Fig.5

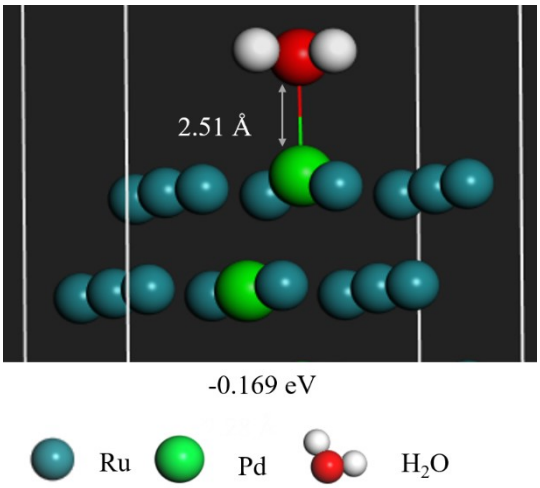

Fig. S8. The stable configurations for H_2O adsorption on c-RuPd as well as corresponding Ru-O bond length and ΔE_{H2O*} values

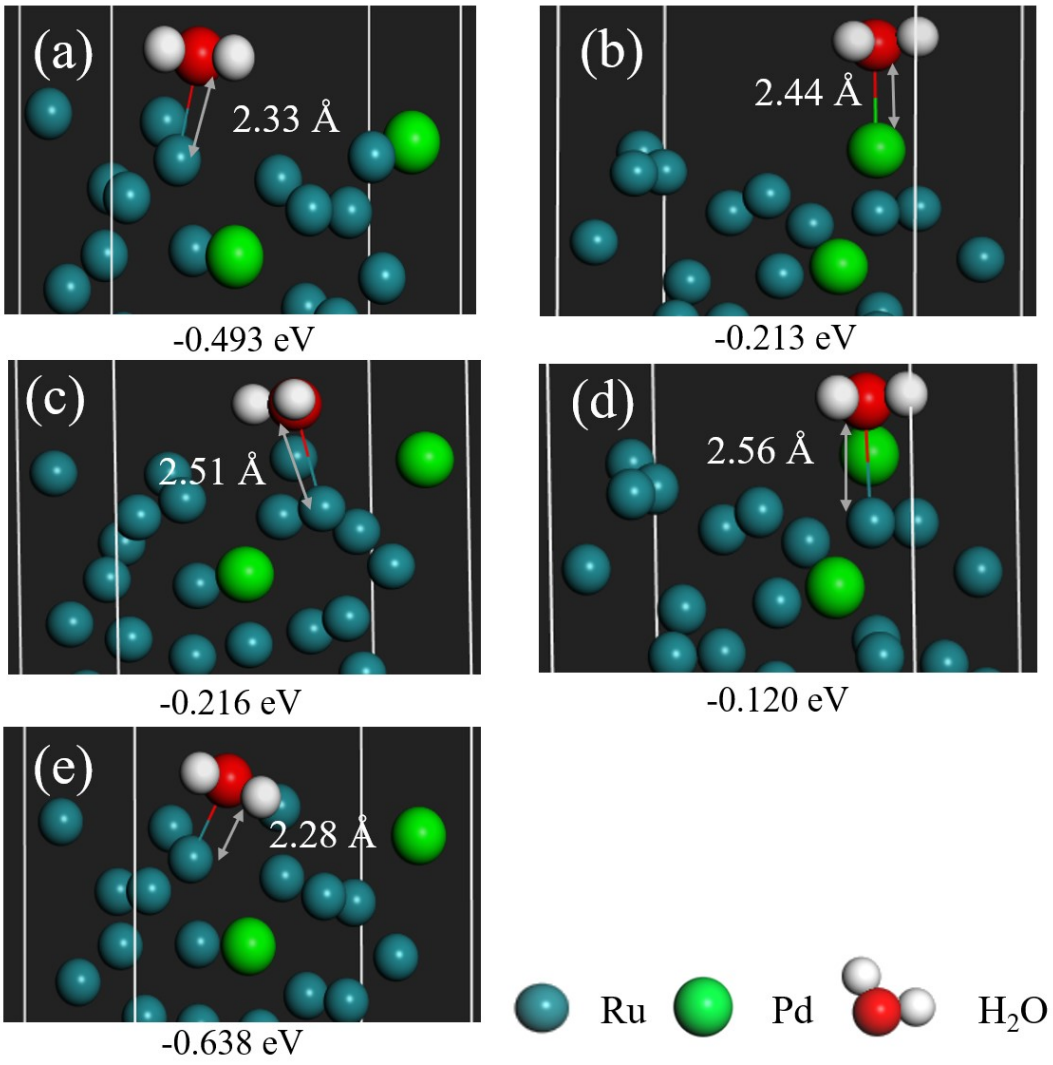

Fig. S9. The stable configurations for H_2O adsorption on am-RuPd as well as corresponding Ru-O bond length and ΔE_{H2O*} values

Table S8. The energy levels of three molecular orbitals for H_2O/Ru(0001), H_2O/c-RuPd and H_2O/am-RuPd. This table corresponds to Fig. 9.

	$1b_1$ (eV)	$3a_1$ (eV)	$1b_2$ (eV)
H_2O/Ru (0001)	-4.94	-6.59	-9.84
H_2O/c-RuPd	-4.93	-6.72	-10.06
H_2O/am-RuPd	-5.40	-6.89	-10.03

Table S9. Adsorption energies (Δ*E*), zero energy difference (ΔZPE), the product of temperature and entropy change (TΔS) and free energy (Δ*G*) of (OH*+H*) and (OH^-+H*) on OH* desorption process.

□	□	ΔE	ΔZPE	TΔS	ΔZPE-TΔS	ΔG
Ru (0001)	OH*+H*	-0.455	-0.048	-0.525	0.477	0.022
	OH^-+H*	-0.443	0.027	-0.208	0.235	-0.208
c-RuPd	OH*+H*	-0.277	-0.079	-0.521	0.442	0.165
	OH^-+H*	-0.542	0.027	-0.208	0.235	-0.307
am-RuPd	OH*+H* (site1)	-1.239	-0.071	-0.489	0.418	-0.821
	OH*+H* (site2)	-0.811	-0.071	-0.489	0.418	-0.393
	OH^-+H*(site1)	-0.760	0.03	-0.1935	0.224	-0.536
	OH^-+H*(site2)	-0.753	0.03	-0.1935	0.224	-0.529

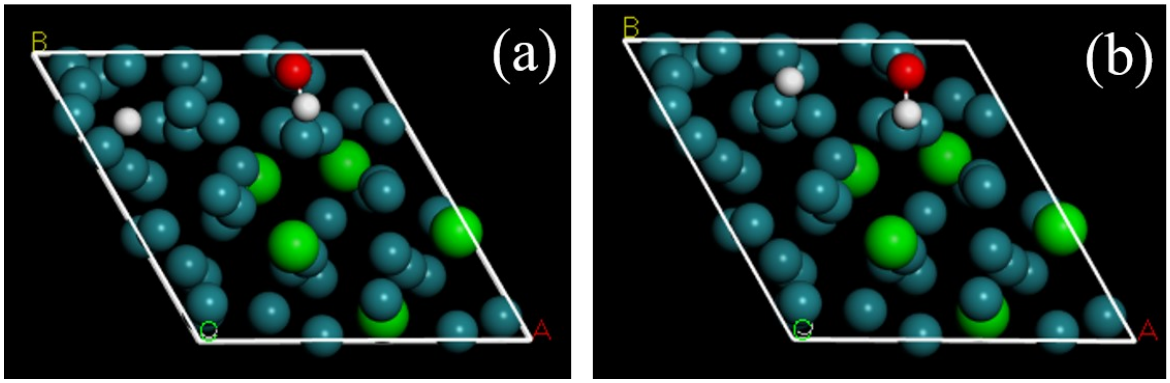

Fig.S9. The adsorption of OH* and H* on (a) am-RuPd-site 1 and (b) am-RuPd-site 1 for OH* desorption process

References

[1] Nørskov J K, Bligaard T, Logadottir A, Kitchin J R, Chen J G, Pandelov S, Stimmingc U,T. rends in the Exchange Current for Hydrogen Evolution. *J. Electrochem. Soc.* 2005;*152*:J23-J26.