Supporting Information for

# Robust Phase Control through Hetero-Seeded Epitaxial Growth for Face-Centered Cubic Pt@Ru Nano-Tetrahedrons with Superior Hydrogen Electro-Oxidation Activity

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## Synthesis of Ru NSs:

Ru NSs were synthesized with the hydrothermal method based on our previous report.<sup>1</sup> The reaction solution contained 0.12 mmol of RuCl<sub>3</sub> xH<sub>2</sub>O, 140 mg of sodium malonate (Na<sub>2</sub>C<sub>3</sub>H<sub>2</sub>O<sub>4</sub> H<sub>2</sub>O), 100 mg of PVP and 0.4 mL of HCHO solution and the volume was 15 mL. The hydrothermal reaction was kept at 160 °C for 8 h and the post-treatment procedure was the same for the synthesis of Pt@Ru NCs.

# Tables:

**Table S1.** The molar ratio of Pt:Ru in the feedstock and in the synthesized Pt@Ru NCs obtained from EDS and ICP-AES analyses.

Sample name	Pt:Ru molar ratio			
	Feedstock	ICP-AES	EDS	
Pt <sub>5</sub> @Ru <sub>95</sub>	5:95	5:95	4:96	
Pt <sub>10</sub> @Ru <sub>90</sub>	10:90	10:90	10:90	
Pt <sub>20</sub> @Ru <sub>80</sub>	20:80	19:81	21:79	
Pt <sub>50</sub> @Ru <sub>50</sub>	50:50	47:53	51:49	

**Table S2.** The molar ratio of Pd:Ru and Rh:Ru in the feedstock and in the two-step synthesized Pd@Ru and Rh-Ru alloy NCs obtained from EDS and ICP-AES analyses.

Sample name	Pd(or Rh):Ru m	Pd(or Rh):Ru molar ratio			
	Feedstock	ICP-AES	EDS		
One-step	20:80	19:81	<i>a</i>		
Pd-Ru NCs					
One-step	20:80	21:79	22:78		
Rh-Ru NCs					
Two-step	20:80	21:79	23:77		
Pd-Ru NCs					
Two-step	20:80	20:80	17:83		
Rh-Ru NCs					

<sup>*a*</sup> Since isolated Pd and Ru NCs were obtained with one-step method and the two kinds of NCs were not evenly distributed, the results of EDS analysis at different regions varied seriously.

Sample	Phase	Lattice constant (nm)	wt.%
One-step Pd-Ru NCs <sup>b</sup>	fcc Pd	3.896(6)	28
	hcp Ru	2.716(5), 4.351(8)	72
One-step Rh-Ru NCs <sup>c</sup>	<i>hcp</i> alloy	2.706(4), 4.316(6)	100
Two-step Pd-Ru NCs <sup>d</sup>	fcc Pd	3.900(2)	20
	fcc Ru	3.845(1)	62
	hcp Ru		18
Two-step Rh-Ru NCs <sup>e</sup>	<i>fcc</i> alloy	3.827(1)	96
	hcp Ru		4

**Table S3.** Rietveld analysis of Pd-Ru and Rh-Ru bimetallic NCs synthesized with one-step and two-step methods. <sup>*a*</sup>

<sup>*a*</sup> The XRD spectra of Pd-Ru and Rh-Ru NCs synthesized with the one-step method were shown in Figure S5c and those of Pd-Ru and Rh-Ru NCs synthesized with the two-step method were shown in Figure 4c. <sup>*b*</sup> *fcc* phase of Pd and *hcp* phase of Ru were included in the refinement and all lattice parameters were relaxed. <sup>*c*</sup> *hcp* phase of Rh<sub>20</sub>Ru<sub>80</sub> random alloy was introduced. Preferential orientation of [0002] direction was taken into consideration in the refinement. *fcc* phase of Rh had no contribution to the spectrum. <sup>*d*</sup> *fcc* phase of Pd, *fcc* phase of Ru and *hcp* phase of Ru were introduced in the refinement. The lattice parameters of two *fcc* phases were relaxed. <sup>*e*</sup> *fcc* phase of Rh<sub>20</sub>Ru<sub>80</sub> random alloy and *hcp* phase of Ru were introduced in the refinement. The lattice parameters of Ru were introduced in the refinement. The lattice parameters of Ru were introduced in the refinement. The lattice phase of Ru were introduced in the refinement. The lattice phase of Ru were introduced in the refinement. The lattice parameters of Ru were introduced in the refinement. The lattice phase of Ru were introduced in the refinement. The lattice phase of Ru were introduced in the refinement. The lattice phase of Ru were introduced in the refinement. The lattice phase of Ru were introduced in the refinement. The lattice phase of Ru were introduced in the refinement. The lattice phase of Ru were introduced in the refinement. The lattice phase was relaxed.

Figures:



Figure S1. TEM and HRTEM images of (a, b) Pt<sub>5</sub>@Ru<sub>95</sub>, (c, d) Pt<sub>20</sub>@Ru<sub>80</sub> and (e, f) Pt<sub>50</sub>@Ru<sub>50</sub>.



Figure S2. Size distribution histograms of Pt@Ru NCs with different compositions.



Figure S3. HAADF-STEM and EDS mapping images of representative NCs in (a)  $Pt_5@Ru_{95}$ , (b)  $Pt_{10}@Ru_{90}$  and (c)  $Pt_{50}@Ru_{50}$ .



**Figure S4.** XRD refinement and component analysis of (a) Pt<sub>5</sub>@Ru<sub>95</sub>, (b) Pt<sub>10</sub>@Ru<sub>90</sub>, (c) Pt<sub>20</sub>@Ru<sub>80</sub> and (d) Pt<sub>50</sub>@Ru<sub>50</sub>. (e) Summary of *R* factors and goodness of fitting.



**Figure S5.** TEM images of (a) pre-synthesized Pt NCs as seeds and (b) fcc Pt@Ru NCs synthesized with the two-step method. (c) HAADF-STEM image and EDS mapping of Pt@Ru NCs synthesized with the two-step method. (d) XRD pattern of fcc Pt@Ru NCs synthesized with the two-step method. The red and blue vertical lines indicate the standard diffraction peaks of fcc Ru (no. 88-2333) and fcc Pt (no. 04-0802), respectively.



**Figure S6.** TEM images of (a) Pd-Ru and (b) Rh-Ru NCs synthesized with the one-step method. Pd multi-twinned particles (MTPs) and Ru nanoplates (NPs) were observed in panel (a) and Rh-Ru alloy NPs were observed in panel (b). The lower part of panel (b) shows the HADDF-STEM image and the corresponding EDS mapping image of a single alloy nanoplate. (c) XRD spectra (black circles) and Rietveld refinement (red curves) of Pd-Ru and Rh-Ru NCs. The fitting results were shown in Table S3.



**Figure S7.** TEM images of (a) a single-crystalline Pd particle, (b) a twinned Pd particle, (c) a single-crystalline Rh particle and (d) a twinned Rh particle used as seeds in the two-step synthesis of Pd-Ru and Rh-Ru bimetallic NCs.



**Figure S8.** TEM images and EDS spectra of (a) *fcc* Pd@Ru NCs and (b) *fcc* Rh-Ru alloy NCs synthesized with two-step method. HRTEM images and corresponding EDS mapping images of (c) a multi-twinned Pd@Ru NC, (d) a single-crystalline Pd@Ru NC with incomplete Ru shell, and (e) a twinned Rh-Ru alloy NC. In the EDS mapping images, red regions represent Pd or Rh and green regions represent Ru.



**Figure S9.** The structure of the interface between (110) facet of *fcc* metal and (110) facet of *fcc* Ru from [1-10] zone-axis. The closest packed layers were labeled as 'A', 'B' and 'C'.



Figure S10. TEM images of carbon black (Vulcan XC-72R) supported Pt@Ru NCs. (a) Pt<sub>5</sub>@Ru<sub>95</sub>/C, (b) Pt<sub>10</sub>@Ru<sub>90</sub>/C, (c) Pt<sub>20</sub>@Ru<sub>80</sub>/C, and (d) Pt<sub>50</sub>@Ru<sub>50</sub>/C.



**Figure S11.** Cu upd stripping curves to determine the ECSA of (a) commercial Pt/C, (b) as-hydrothermally synthesized Ru/C, (c) 500 °C annealed Ru/C, (d-g) Pt@Ru NCs/C, (h) Pd@Ru NCs/C and (i) Rh-Ru alloy NCs/C. The electrode was first kept at 0.01 V in N<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> solution for 100 s to reduce all the sites on the catalysts and then kept at 0.3 V for 100 s in 2 mM Cu(ClO<sub>4</sub>)<sub>2</sub> + 0.1 M HClO<sub>4</sub> solution (solid curves) or in 0.1 M HClO<sub>4</sub> solution (dashed curves), followed by the collection of CV curves from 0.3 V to 0.9 V with the sweep rate of 50 mV s<sup>-1</sup>. The difference between solid and dashed curves in the anodic sweep corresponds to the stripping current of upd Cu, and the ECSA of the sample was calculated from the stripping charge with the coefficient of 420  $\mu$ C·cm<sup>-2</sup>.<sup>2</sup>



**Figure S12.** Ag upd stripping curves to analyze the surface compositions of (a) commercial PtRu alloy/C, (b-d) Pt@Ru NCs/C, (e) Pd@Ru NCs/C and (f) Rh-Ru alloy NCs/C. The electrode was first kept at 1.1 V in N<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> solution for 100 s to pre-oxidize all sites on surface, and then kept at 0.66 V in 1 mM AgClO<sub>4</sub> + 0.1 M HClO<sub>4</sub> solution (solid curves) or 0.1 M HClO<sub>4</sub> solution (dashed curves) for another 100s, followed by CV sweep between 0.66 V and 1.2 V with the scan rate of 50 mV s<sup>-1</sup>. The difference between solid and dashed curves in the anodic sweeps is the stripping current of upd Ag.



**Figure S13.** (a) Polarization curves with iR-compensation obtained on  $Pt_{10}@Ru_{90}/C$  with different rotation rates in 0.1 M HClO<sub>4</sub> aqueous solution saturated with H<sub>2</sub>. Sweep rate: 5 mV s<sup>-1</sup>; temperature: 25 °C; loading of total metal mass: 3 µg. (b) Koutecky-Levich plot derived from the polarization curves in panel (a). The exchange electron number (*n*) and kinetic current at different potentials were determined by fitting the plots with Kouteck-Levich equation:

$$I^{-1} = I_{d}^{-1} + I_{k}^{-1} = \frac{1}{B\omega^{1/2}} + I_{k}^{-1} = \frac{1}{0.20nFAD^{2/3}v^{-1/6}c_{0}}\omega^{-1/2} + I_{k}^{-1}$$
(S1)

where  $I_k$  and  $I_d$  are the kinetic current and diffusion limited current, *F* is Faraday constant, *A* is the electrode area (0.196 cm<sup>2</sup>), *D* is the H<sub>2</sub> diffusion coefficient in 0.1 M HClO<sub>4</sub> solution, *v* is the kinematic viscosity,  $c_0$  is the solubility of H<sub>2</sub> in the electrolyte, and  $\omega$  is the rotation rate in rpm.<sup>3</sup>



Figure S14. TEM image of Pt<sub>10</sub>@Ru<sub>90</sub>/C after the electrochemical test.



**Figure S15.** (a) CV curves of Pd@Ru NCs/C (black) and Rh-Ru alloy NCs/C (red) in N<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> solution. The scan rate was 50 mV s<sup>-1</sup>. The current density was normalized to the ECSA of the catalysts deduced from the Cu upd stripping curves. (b) Polarization curves obtained on Pd@Ru NCs/C (black) and Rh-Ru alloy NCs/C (red) in 0.1 M HClO<sub>4</sub> aqueous solution saturated with H<sub>2</sub>. Sweep rate: 5 mV s<sup>-1</sup>; rotation speed: 2500 rpm; temperature: 25 °C; loading of total metal mass: 3  $\mu$ g. (c) Specific surface area (SSA) deduced from Cu upd stripping curves and ICP-AES (top), mass-normalized exchange current densities (middle) and ECSA-normalized exchange current densities (bottom) of Pd@Ru NCs/C and Rh-Ru alloy NCs/C.



**Figure S16.** (a) TEM, (b) HRTEM images and (c) size distribution histogram of the as-prepared Ru/C. (d) TEM, (e) HRTEM images and (f) size distribution histogram of the Ru/C annealed at 500 °C in N<sub>2</sub> for 5 h. The inset of panel (e) shows the corresponding FFT pattern, in accord with the reciprocal lattice of *hcp* phase. (g) XRD pattern of the as-prepared Ru/C (red) and the annealed Ru/C (blue). The black vertical lines indicate the standard diffraction peaks of *hcp* Ru (no. 06-0663).



**Figure S17.** XPS spectra of Ru 3p electrons of  $Pt_{10}@Ru_{10}$  (black) and the as-prepared Ru NSs (red) after the hydrothermal synthesis and post-treatment (dialysis, centrifugation and vacuum drying). The blue and pink vertical dashed lines represent the reported binding energy of Ru 3p electrons in metallic Ru and RuO<sub>2</sub>, respectively.<sup>4,5</sup> The binding energy of Ru 3p electrons in the as-prepared Ru NSs was higher than that of  $Pt_{10}@Ru_{90}$ , indicating that the surface oxidation level was higher on the as-prepared Ru NSs.



**Figure S18.** CV curves of the Pt@Ru NCs/C (solid curves), the as-prepared Ru/C (black dashed curve) and the annealed Ru/C (dark yellow dashed curve) in  $N_2$  saturated 0.1 M HClO<sub>4</sub> solution. The sweep rate was 50 mV s<sup>-1</sup>. The current density was normalized to the ECSA of each catalyst.

#### **Computation section:**

The lattice parameters and energy of *fcc* Ru (Z = 4) and *hcp* Ru (Z = 2) unit cells were firstly calculated by using (11×11×11) and (13×13×11) K-point grids, respectively. The optimized lattice parameters, a = 3.82 Å for *fcc* Ru and a = 2.72 Å and c = 4.31 Å for *hcp* Ru, were used to build the supercells in the following.

The energy to imbed an M atom (M = Pt, Pd and Rh) into hcp Ru lattice was calculated according to following equation:

E = E(M-Ru) + E(M) - E(Ru-Ru) - E(Ru) (S2) In this equation, E(M-Ru) and E(Ru-Ru) were the energy of a (2×2×1) *hcp* Ru supercell with a Ru atom replaced by M atom and without the substitution, respectively, and E(M) and E(Ru) were the energy of an M and a Ru atom in bulk.

The supercells of the slabs used to calculate the surface formation energy of (111) and (100) facets of *fcc* Ru contained eight layers of Ru atoms. First, the outer three layers of Ru atoms on each side of the slab were allowed to relax with CG method, followed by the calculation of the total energy. The surface formation energy ( $\sigma_s$ ) was then calculated with the following equation:

$$\sigma_{\rm s} = (E_{\rm slab} - n \, E_{\rm Ru}) \,/\, 2A \tag{S3}$$

where  $E_{\text{slab}}$  was the total energy of a supercell of the slab,  $E_{\text{Ru}}$  was the calculated energy per Ru atom in bulk, *n* was the number of Ru atoms in one supercell of the slab and *A* was the cross-section area of the supercell.

Figure S18 shows the supercells used to calculate the interface formation energy, in which green balls represent Ru atoms and blue balls represent M (M = Pt, Pd or Rh) atoms. Model a and b show the supercells including (100) interface and (111) interface between *fcc* Ru and *fcc* M, respectively, and Model c-f show the corresponding mono-metallic supercells. The lattice constants (*a* and *c*) of Model a and b were optimized and the z-positions of atoms in Model a and b were allowed to relax. Model c and d had the same lattice constant *a* with Model a, and Model e and f had the same lattice constant *a* with Model b. The lattice constants *c* of these supercells were optimized. The interface formation energies ( $\sigma_i$ ) of (100) and (111) interface were then calculated with the following equations:

$$\sigma_{\rm i}(100) = (E_{\rm a} - E_{\rm c} - E_{\rm d}) / 2A \tag{S4}$$

$$\sigma_{\rm i}(111) = (E_{\rm b} - E_{\rm e} - E_{\rm f}) / 2A \tag{S5}$$

where  $E_x$  (x = a-f) was the total energy of Model x and A was the cross-section area of the corresponding supercell.



Figure S19. The supercells used to calculate the interface formation energy between

*fcc* Ru (green balls) and *fcc* M (blue balls, M = Pt, Pd, Rh). (a, b) Supercells including two (100) interfaces and two (111) interfaces, respectively. (c-f) Mono-metallic supercells.

To understand the effect of surface structure on the surface oxidation level at small overpotential for HOR, namely potential slightly higher than 0 V vs RHE, and consequently the influence on the HOR activity, we calculated the free energy for the oxygen adsorption at 0 V ( $\Delta G_0$ ) and the dissociated adsorption free energy of a hydrogen atom on surface ( $\Delta G_H$ ).  $\Delta G_0$  and  $\Delta G_H$  correspond to the free energy change of following two reactions respectively:

\* + H<sub>2</sub>O (*l*) 
$$\rightarrow$$
 O\* + 2H<sup>+</sup> + 2e<sup>-</sup> (S6)

$$* + 1/2H_2(g) \to H^* \tag{S7}$$

\* stands for an empty site on surface, and O\* and H\* for a site occupied by O atom and H atom respectively. Therefore,  $\Delta G_0$  and  $\Delta G_H$  can be calculated with the following equations:

$$\Delta G_{\rm O} = G({\rm O}^*) + 2G({\rm H}^+ + {\rm e}^{-}) - G({\rm H}_2{\rm O})$$
(S8)

$$\Delta G_{\rm H} = G({\rm H}^*) - G(^*) - 1/2G({\rm H}_2)$$

In these equations,  $G(^*)$ ,  $G(O^*)$  and  $G(H^*)$  are the free energies of supercells of the slabs without adsorbate, with an adsorbed O atom and with an adsorbed H atom, respectively.  $G(H_2O)$  and  $G(H_2)$  are the free energies of  $H_2O$  and  $H_2$  molecules. At 0 V vs RHE, the reaction 1/2 H<sub>2</sub>  $\rightarrow$ H<sup>+</sup> + e<sup>-</sup> is in equilibrium. Namely,

(S9)

$$1/2G(H_2) = G(H^+ + e^-)$$
(S10)

Therefore,

G =

$$\Delta G_0 = G(O^*) + G(H_2) - G(^*) - G(H_2O)$$
(S11)

The standard formula of Gibbs free energy (G) is:

$$E + ZPE + \delta H_0 - TS \tag{S12}$$

In this formula, *E* and ZPE are the DFT-calculated single point energy (SPE) and zero point energy of a relaxed structure.  $\delta H_0$  and *TS* are the integrated heat capacity and the product of temperature (*T*) and entropy (*S*) at 298 K. For the calculation of surface species, ZPEs,  $\delta H_0$  and *TS* of adsorbates were included, while those of Ru slabs and clusters were neglected, since these values were relatively small and could be effectively canceled in the calculation of adsorption free energy.<sup>6-8</sup>  $\delta H_0$  and *TS* for gas-phase H<sub>2</sub>, H<sub>2</sub>O and adsorbates at 298 K were taken from the Ref. 6. For liquid-phase H<sub>2</sub>O, considering that the vapor pressure of H<sub>2</sub>O at 298 K is 0.035 atm, the Gibbs free energy was calculated according to:

$$G(H_2O, l, T) = G(H_2O, g, p, T) = G(H_2O, g, p_0, T) + k_BT\ln(p/p_0)$$
(S13)

In this equation,  $p_0$  is 1 atm and p is the vapor pressure of H<sub>2</sub>O. Table S4 lists the thermodynamic data of H<sub>2</sub>, H<sub>2</sub>O and adsorbates.

	E	ZPE	$\delta H_0$	TS	G
$H_2(g)$	-6.770	0.216	0.09	0.42	-6.884
$H_2O(l)$	-14.219	0.552	0.10	0.65	-14.217
O*			0.025	0.038	
H*			0.005	0.007	

Table S4. Thermodynamic data (unit: eV) of H<sub>2</sub>, H<sub>2</sub>O, O\* and H\* at 298 K.

The slab models of (111) and (100) facets of *fcc* Ru and (0001), (10-10) and (10-11) facets of *hcp* Ru, and amorphous Ru<sub>50</sub> clusters were involved in the calculation. The insets of Figure 7a show the relaxed structures of the supercells of Ru slabs and a representative amorphous Ru<sub>50</sub> cluster without adsorbates. Each supercell of slab contained 48 Ru atoms in 6 layers and 15 Å of vacuum layer, and top three layers of Ru atoms were allowed to move in all relaxation procedures. Box of  $30 \times 30 \times 30$  Å<sup>3</sup> was used in the calculation on clusters. To construct an amorphous Ru<sub>50</sub> cluster, an *hcp* Ru<sub>50</sub> cluster was first built up, followed by ab initio MD at 3000 K and ionic relaxation with CG method. Five amorphous Ru<sub>50</sub> clusters were constructed by varying the step number of MD, and the average of the calculated data on these clusters were finally used.

The formation energies of half-coverage and full-coverage oxygen adsorption layer on Ru slabs were calculated. The sites for the oxygen adsorption were determined by comparing the SPEs of different adsorption configurations. Figure S19a-j shows the relaxed structure of Ru slabs with the oxygen adsorption layers. Oxygen atoms preferentially occupied the *hcp* sites on (111) facet of *fcc* Ru and (0001) facets of *hcp* Ru, triple sites on (10-11) facets of *hcp* Ru, bridge sites on (10-10) facet of *hcp* Ru and quadruple sites on (100) facet of *fcc* Ru. 28 oxygen atoms were added on the surface of one Ru<sub>50</sub> amorphous cluster as the adsorption layer and the thermodynamically favored configuration was obtained through simulated annealing, as shown in Figure S19k. Table S5 lists the value of  $\Delta G_0$  obtained on each structure. All the values of  $\Delta G_0$  obtained on the slabs with full-coverage oxygen were larger than 0, indicating full-coverage oxygen layer would not form on Ru slabs at 0 V vs RHE.



**Figure S20.** Relaxed structures of Ru slabs with (a-e) half-coverage oxygen adsorption layer and with (f-j) full-coverage oxygen adsorption layer, and (k) a representative amorphous  $Ru_{50}$  cluster adsorbed 28 oxygen atoms. Blue balls stand for Ru atoms and red ones for O atoms. The black frames in panel (a-j) indicate the supercells used in the DFT calculations.

Slab	Coverage	$E_{O^*,DFT}$ <sup>a</sup>	ZPE <sub>0*</sub> <sup>b</sup>	$E_{0,\text{DFT}}^{c}$	$\Delta G_0$
(111) of <i>fcc</i>	50 %	-449.884	0.312	-421.168	0.219
	100 %	-475.776	0.768		0.590
(100) of <i>fcc</i>	50 %	-444.508	0.112	-414.376	-0.185
	100 %	-467.884	0.336		0.674
(0001) of <i>hcp</i>	50 %	-454.040	0.300	-425.004	0.139
	100 %	-479.972	0.744		0.542
(10-11) of <i>hcp</i>	50 %	-452.468	0.320	-422.212	-0.164
	100 %	-476.984	0.632		0.552
(10-10) of <i>hcp</i>	50 %	-450.420	0.264	-420.464	-0.103
	100 %	-471.192	0.536		1.064
Amorphous Ru <sub>50</sub> clusters		-592.154	1.932	-379.438	-0.208
		-592.308	1.642	-379.098	-0.236
		-592.156	1.802	-379.206	-0.221
		-592.421	1.883	-378.746	-0.244
		-592.059	1.701	-378.986	-0.229
		Average <sup>d</sup>		-379.095	-0.228
				$\pm 0.257$	$\pm 0.014$

**Table S5.** The free energies (unit: eV) for the formation of oxygen adsorption layer on Ru slabs and amorphous clusters normalized to the number of oxygen atoms.

<sup>*a*</sup> SPE of supercell with adsorbed oxygen atoms. <sup>*b*</sup> The sum of ZPEs of all adsorbed oxygen atoms. <sup>*c*</sup> SPE of supercell without adsorbed oxygen atoms. <sup>*d*</sup> Average data on five Ru<sub>50</sub> amorphous clusters.

The dissociated adsorption energies of one hydrogen atom on all the slabs and clusters with and without adsorbed oxygen were then calculated. The adsorption site for hydrogen atom was first optimized by comparing the SPEs of different adsorption configurations. Figure S20 shows the relaxed structures with the adsorbed hydrogen atom and Table S6-S7 lists the  $\Delta G_{\rm H}$  values calculated from these structures.



**Figure S21.** Relaxed adsorption structure of hydrogen atom on Ru slabs and amorphous cluster (a-f) without and (g-l) with the adsorbed oxygen atoms. Blue balls stand for Ru atoms, red ones for O atoms and white ones for H atoms.

	$E_{\mathrm{H}^*,\mathrm{DFT}}{}^a$	$ZPE_{H^*}{}^b$	$\Delta G_{ m H}$		
(111) of <i>fcc</i>	-424.889	0.184	-0.097		
(100) of <i>fcc</i>	-418.218	0.100	-0.302		
(0001) of <i>hcp</i>	-428.736	0.180	-0.112		
(10-11) of <i>hcp</i>	-426.014	0.173	-0.189		
(10-10) of <i>hcp</i>	-424.350	0.168	-0.278		
Amorphous Ru <sub>50</sub>	-383.409	0.163	-0.368		
clusters	-383.123	0.171	-0.414		
	-383.263	0.162	-0.455		
	-382.801	0.173	-0.441		
	-382.981	0.167	-0.388		
	Average		$-0.413 \pm 0.036$		

**Table S6.** The dissociated adsorption energy (unit: eV) of hydrogen on Ru slabs and amorphous clusters without the adsorbed oxygen layer.

<sup>*a*</sup> SPE of supercell with adsorbed hydrogen atom. <sup>*b*</sup> ZPE of the hydrogen atom in the supercell.

**Table S7.** The dissociated adsorption energy (unti: eV) of hydrogen on Ru slabs and amorphous clusters with the adsorbed oxygen layer. <sup>*a*</sup>

	$E_{\text{O*+H*,DFT}}^{b}$	ZPE <sub>O*+H*</sub> , <sup>c</sup>	$\Delta G_{ m H}$
(111) of <i>fcc</i>	-453.402	0.504	0.114
(100) of <i>fcc</i>	-447.879	0.270	0.227
(0001) of <i>hcp</i>	-457.517	0.494	0.145
(10-11) of <i>hcp</i>	-455.825	0.471	0.234
(10-10) of <i>hcp</i>	-453.752	0.426	0.270
Amorphous Ru <sub>50</sub>	-595.427	2.103	0.338
clusters	-595.499	1.805	0.412
	-595.299	1.959	0.454
	-595.638	2.030	0.370
	-595.266	1.865	0.397
	Average		$0.394 \pm 0.044$

<sup>*a*</sup> The coverage of the adsorbed oxygen layer on slab models was 50 %. <sup>*b*</sup> SPE of supercell with adsorbed oxygen and hydrogen atoms. <sup>*c*</sup> The sum of ZPEs of all adsorbed oxygen and hydrogen atoms.

To verify the difference between the energetic data obtained on crystallized slabs and those on amorphous clusters mainly resulted from different crystallinity rather than different 'particle size', we constructed two crystallized clusters, i.e. an *fcc* Ru<sub>56</sub> cluster enclosed by four {111} facets and an *hcp* Ru<sub>69</sub> cluster enclosed by six {10-11} facets, and calculated the values of  $\Delta G_0$  and  $\Delta G_H$  on these clusters. The adsorption configurations of oxygen and hydrogen on these two clusters were same as those on the (111) slab of *fcc* Ru and the (10-11) slab of *hcp* Ru. Figure S21 shows the structures of these clusters without and with adsorbates, and Table S8 shows the adsorption energies obtained on them. The crystallized clusters adsorbed hydrogen S21 only slightly stronger than corresponding slabs, suggesting different crystallinity was the major reason for the different values of  $\Delta G_{\rm H}$  between the crystallized slabs and amorphous clusters.



**Figure S22.** Relaxed structures of (a) *fcc*  $Ru_{56}$  tetrahedron enclosed by four {111} facets and (b) *hcp*  $Ru_{69}$  trigonal bipyramid enclosed by six {10-11} facets without adsorbates, with oxygen adsorption layer, with adsorbed hydrogen atom and with adsorbed hydrogen atom and oxygen layer. The adsorption configurations are as same as those on bare or oxygen half-covered (111) slab of *fcc* Ru and (10-11) slab of *hcp* Ru, respectively. Blue balls stand for Ru atoms, red ones for O atoms and white ones for H atoms.

**Table S8.** The comparison of  $\Delta G_{\rm O}$  and  $\Delta G_{\rm H}$  (unit: eV) among crystallized clusters, crystallized slabs and amorphous cluster.

	1				
	$E_{\rm O^*,DFT}$	ZPE <sub>O*</sub>	$E_{0,\mathrm{DFT}}$	$\Delta G_0$	
fcc Ru <sub>56</sub> cluster <sup>a</sup>	-674.870	2.304	-412.106	0.085	
<i>fcc</i> (111) slab				0.219	
<i>hcp</i> Ru <sub>69</sub> cluster <sup>b</sup>	-750.936	2.325	-523.223	-0.193	
<i>hcp</i> (10-11) slab				-0.164	
Amorphous Ru <sub>50</sub> clust	er			$-0.228 \pm 0.014$	
	$E_{\mathrm{H}^*,\mathrm{DFT}}$	ZPE <sub>H*</sub>	$\Delta G_{ m H}$		
fcc Ru <sub>56</sub> cluster	-415.818	0.160	-0.112		
<i>fcc</i> (111) slab			-0.097		
hcp Ru <sub>69</sub> cluster	-527.035	0.160	-0.212		
<i>hcp</i> (10-11) slab			-0.189		
Amorphous Ru <sub>50</sub> clust	er		-0.413 ±0.036		
	Eo*+H*,DFT	ZPE <sub>O*+H*</sub>	$\Delta G_{ m H}$		
fcc Ru <sub>56</sub> cluster	-678.389	2.484	0.101		
<i>fcc</i> (111) slab			0.114		
hcp Ru <sub>69</sub> cluster	-754.312	2.468	0.209		
<i>hcp</i> (10-11) slab			0.234		
Amorphous Ru <sub>50</sub> cluster			0.394 ±0.044		

<sup>*a*</sup> This cluster exposed four  $\{111\}$  facets and adsorbed 36 oxygen atoms. The adsorption configuration was the same as that on (111) slab of *fcc* Ru with s22

half-coverage oxygen layer. <sup>b</sup> This cluster exposed six {10-11} facets and adsorbed 30 oxygen atoms. The adsorption configuration was the same as that on (10-11) slab of hcp Ru with half-coverage oxygen layer.

To understand the lattice extension effect derived from the Pt cores on the HOR activity of the *fcc* Ru shells, we calculated the values of  $\Delta G_0$  and  $\Delta G_H$  on the laterally stretched (111) slabs of *fcc* Ru. The highest stretching ratio was 4.1 %, corresponding to the DFT-optimized lattice parameter of *fcc* Pt (a = 3.98 Å). Table S9 shows the calculation results. The values of  $\Delta G_0$  were positive with all stretching ratios, suggesting the adsorbed oxygen layer would not form on the stretched (111) slabs of *fcc* Ru at 0 V. Thus, we only calculated the values of  $\Delta G_H$  on the unpassivated slabs.

Stretching  $E_{0,\text{DFT}}$ ZPE<sub>0\*</sub>  $ZPE_{H^*}$ EO\*,DFT  $\Delta G_{\rm O}$  $E_{\mathrm{H}^*,\mathrm{DFT}}$  $\Delta G_{
m H}$ ratio (%) 0 -449.884 -421.168 0.312 0.219 -424.889 0.184 -0.097 0.4 -421.120 -449.946 0.308 0.183 -424.869 0.183 -0.126 1.0 -420.968 -449.964 0.152 -424.728 0.306 0.182 -0.138 2.1 -419.784 -448.938 0.306 0.108 -423.561 0.181 -0.156 -447.496 3.1 -418.272 0.296 0.088 -422.061 0.180 -0.169

0.011

0.292

-420.134

0.178

-0.188

**Table S9.** Calculated energy data on stretched (111) slabs of *fcc* Ru with different stretching ratios.

4.1

-416.328

-445.856

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