

Oxygen-modified Supra-nanometer-sized RuPt for Robust Alkaline HER/HOR

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10 # Equal contribution.

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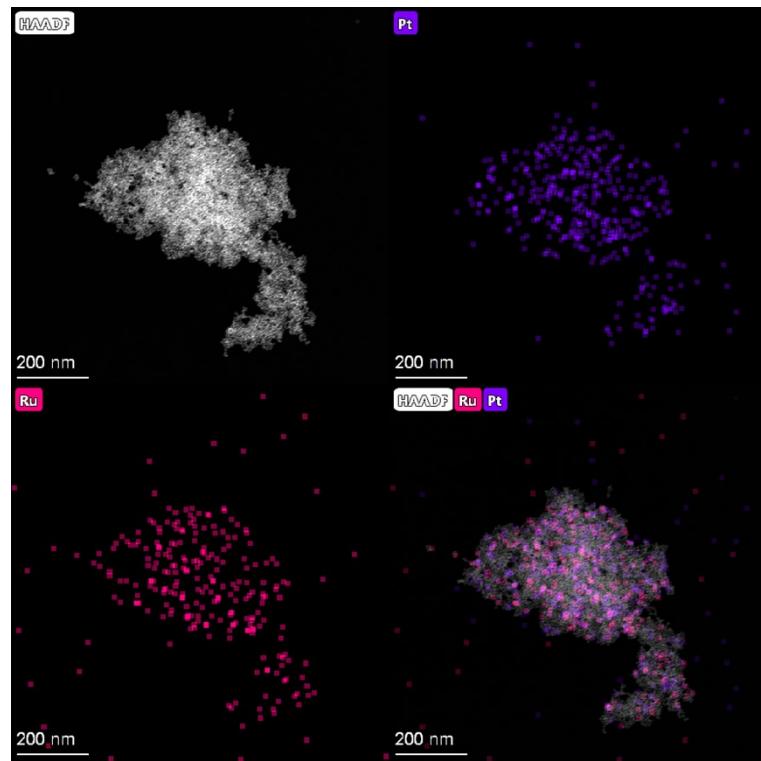
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39 **Fig. S1** The EDS mapping of RuPt.

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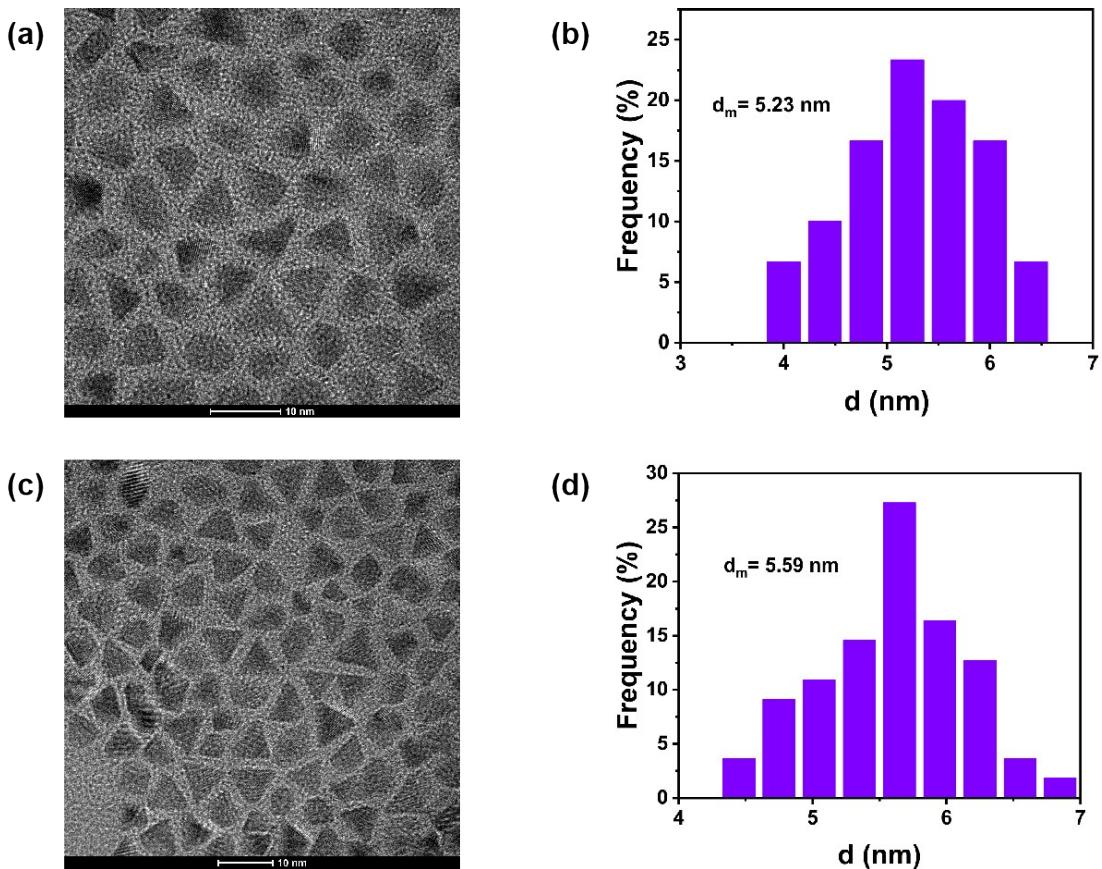
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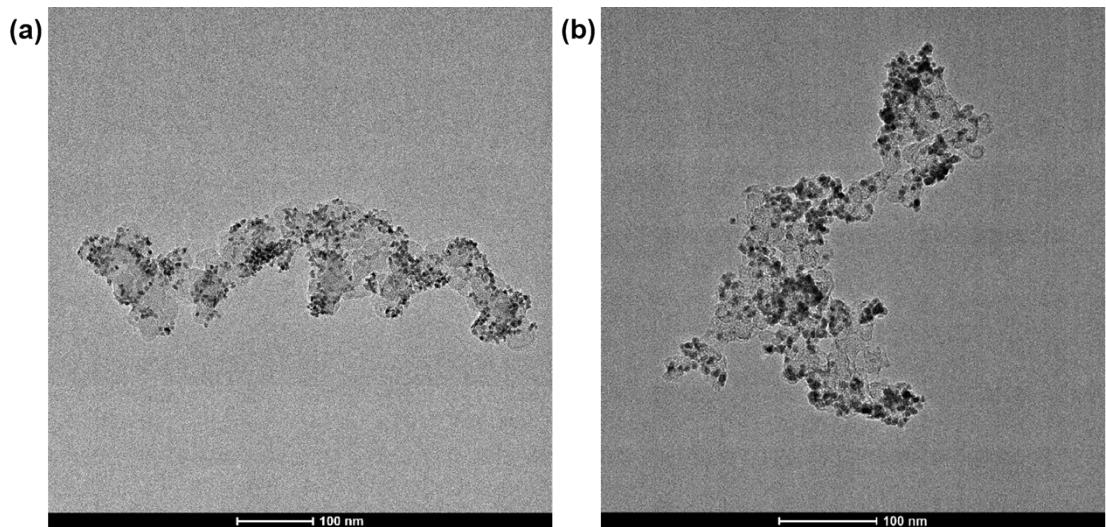
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56 **Fig. S2** (a) TEM image and (b) corresponding size distribution diagram of supra-
57 nanometer-sized RuPt nanocrystals synthesized with a reaction time of 0.5 h. (c) TEM
58 image and (d) corresponding size distribution diagram of supra-nanometer-sized RuPt
59 nanocrystals synthesized with a reaction time of 1.5 h.
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79 **Fig. S3** TEM images of (a) RuPt/C-180 and (b) RuPt/C-220.

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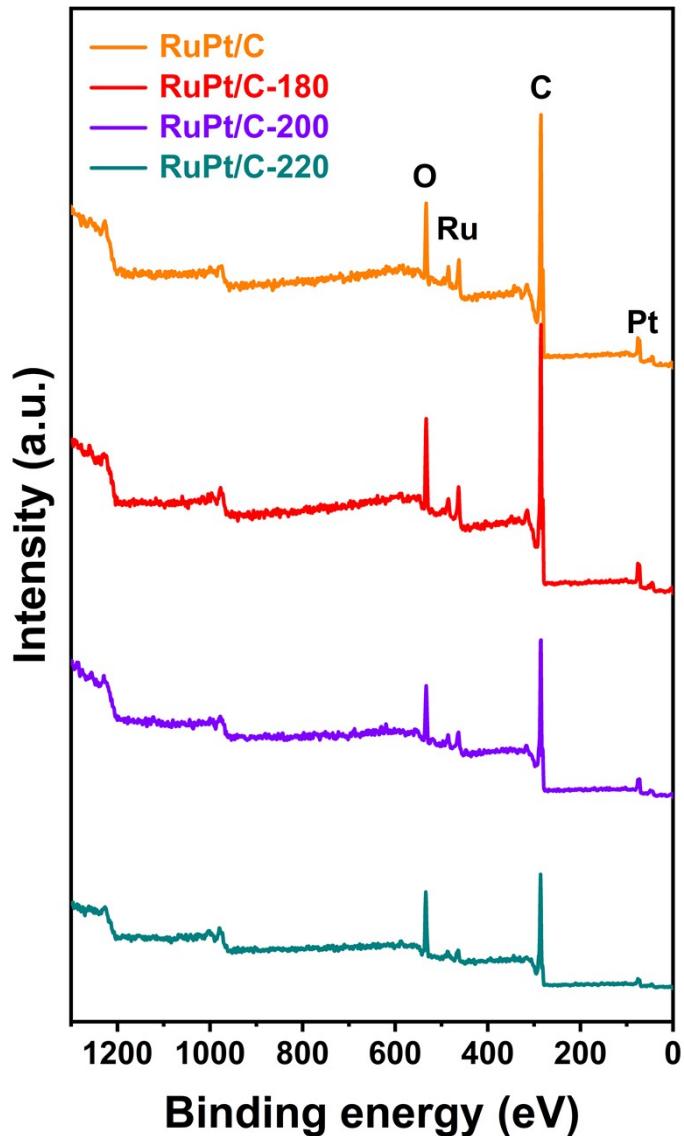
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106 **Fig. S4** XPS full spectra of RuPt/C, RuPt/C-180, RuPt/C-200, and RuPt/C-220.

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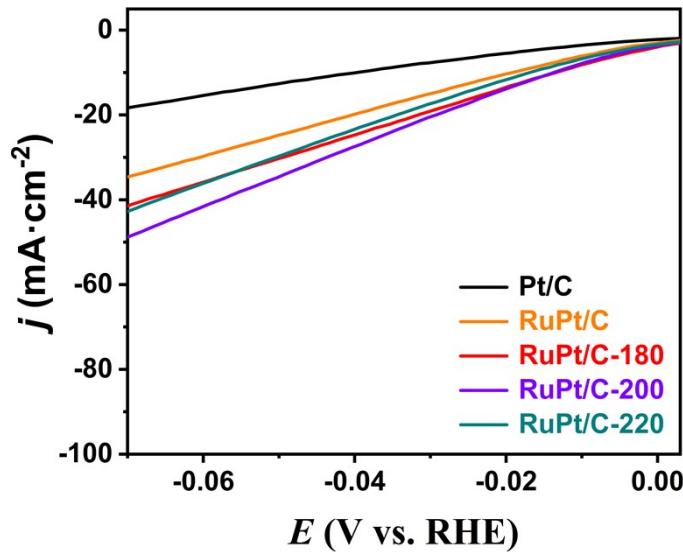
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123 **Fig. S5** HER polarization curves of commercial Pt/C, RuPt/C, RuPt/C-180, RuPt/C-
 124 200, and RuPt/C-220 without iR correction in a N_2 -saturated 1 M KOH electrolyte
 125 with a rotating speed of 1,600 rpm.

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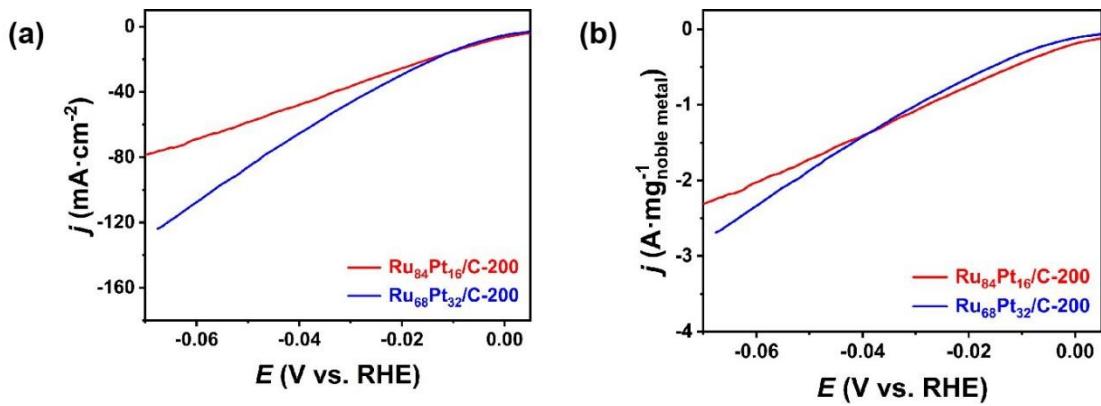
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145 **Fig. S6** (a) HER polarization curves of $\text{Ru}_{84}\text{Pt}_{16}/\text{C-200}$ (with less Pt) and $\text{Ru}_{68}\text{Pt}_{32}/\text{C-}$
 146 200 (with less Ru) in a N_2 -saturated 1 M KOH electrolyte with a rotating speed of
 147 1,600 rpm. (b) Corresponding Mass-normalized HER polarization curves in (a).

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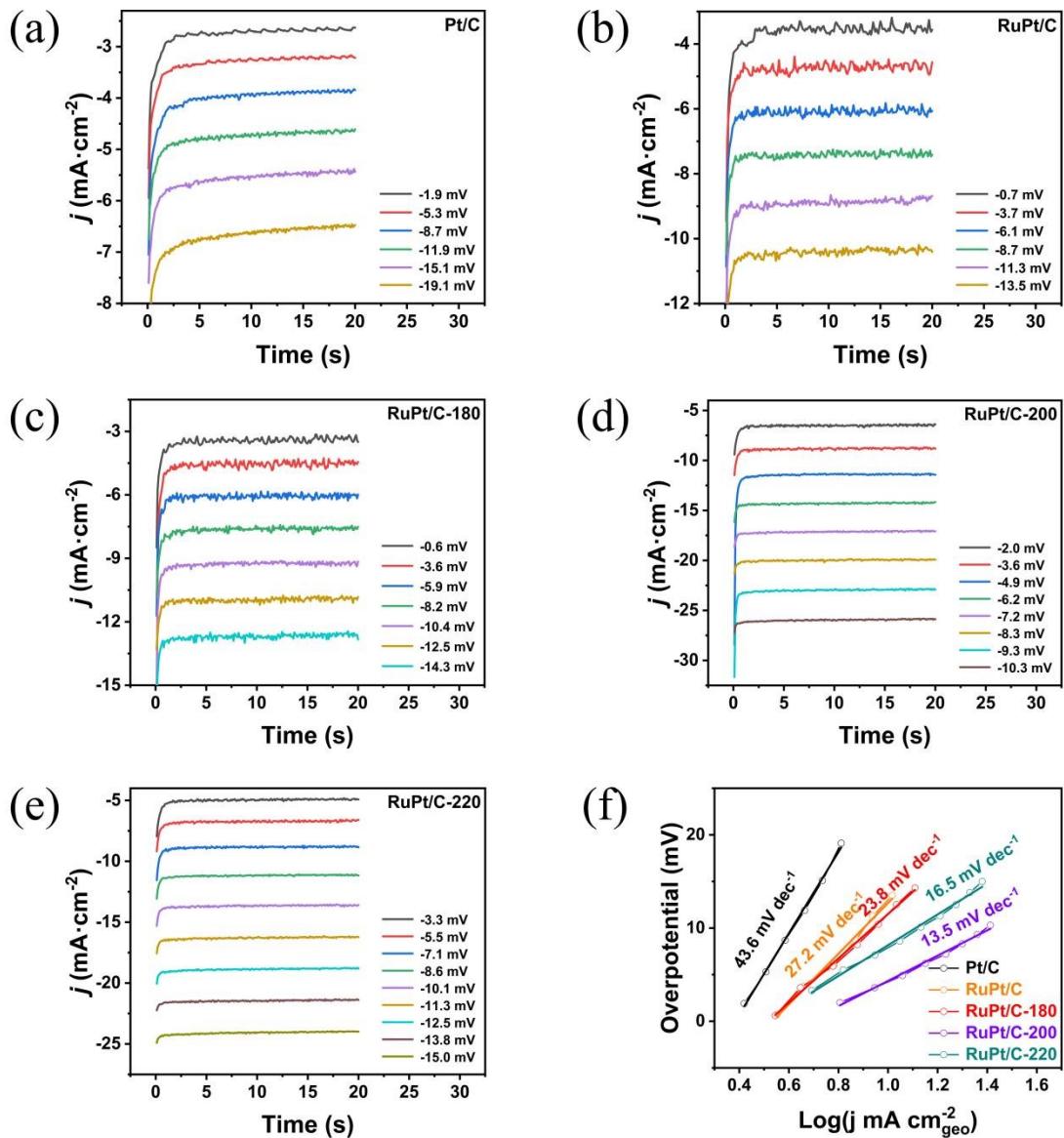
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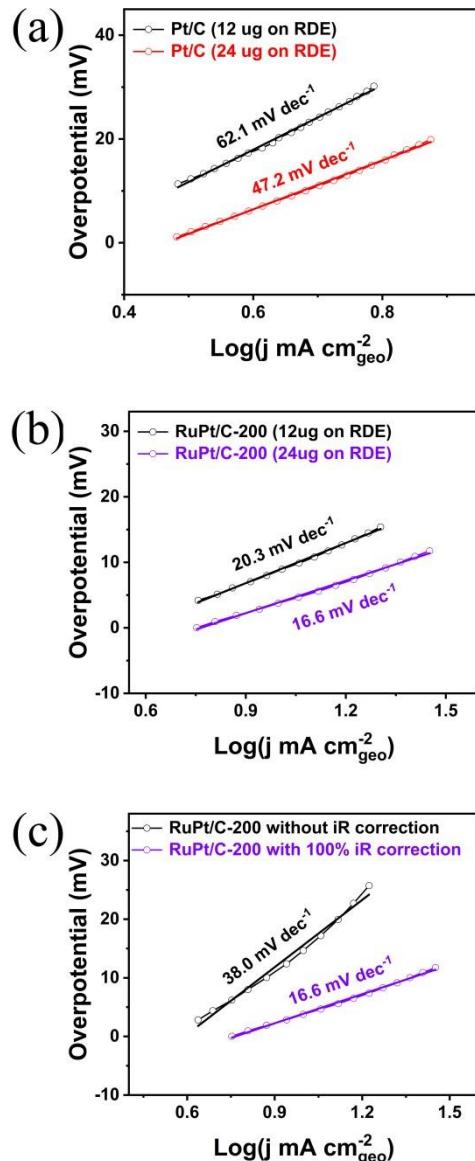
156 **Fig. S7** Chronoamperometry study of (a) Pt/C, (b) RuPt/C, (c) RuPt/C-180, (d)
157 RuPt/C-200 and (e) RuPt/C-220 at different applied potentials vs RHE for the HER in
158 1 M KOH solution (f) Tafel slopes derived from (a), (b), (c), (d) and (e).

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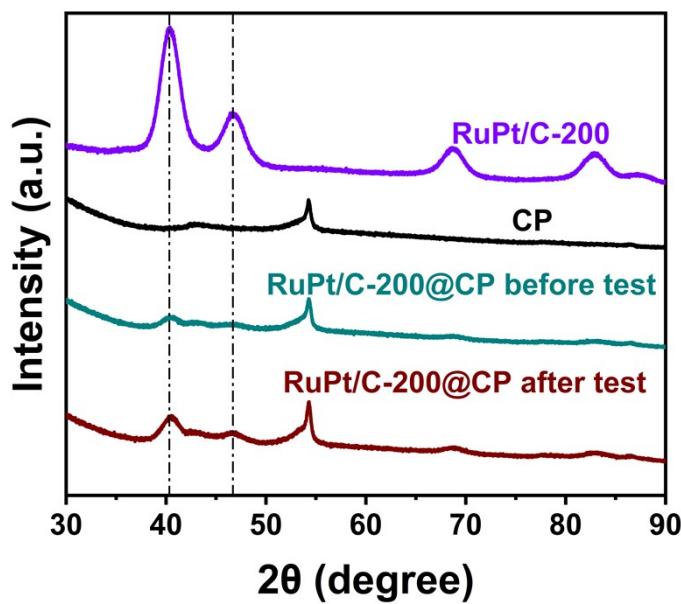
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164 **Fig. S8** (a) Tafel slopes of 12 µg and 24 µg Pt/C tested on a 0.196 cm² rotating disk
165 electrode. (b) Tafel slopes of 12 µg and 24 µg RuPt/C-200 tested on a 0.196 cm²
166 rotating disk electrode.(c) Tafel slopes of RuPt/C-200 (24 µg on a 0.196 cm² rotating
167 disk electrode) catalyst without *iR* potential compensation and with 100% *iR* potential
168 compensation. (The Tafel slope is calculated from the LSV curve unless otherwise
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178 **Fig. S9** XRD patterns of RuPt/C-200, CP, RuPt/C-200@CP before stability
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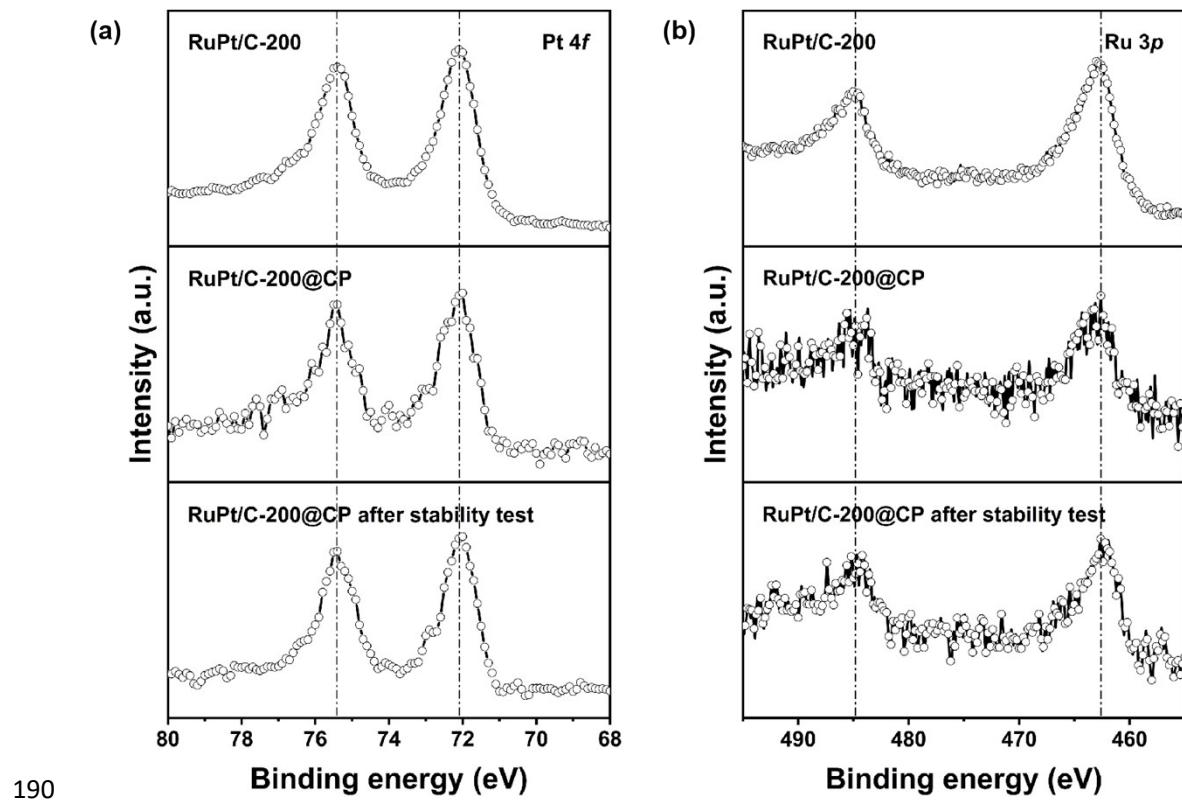
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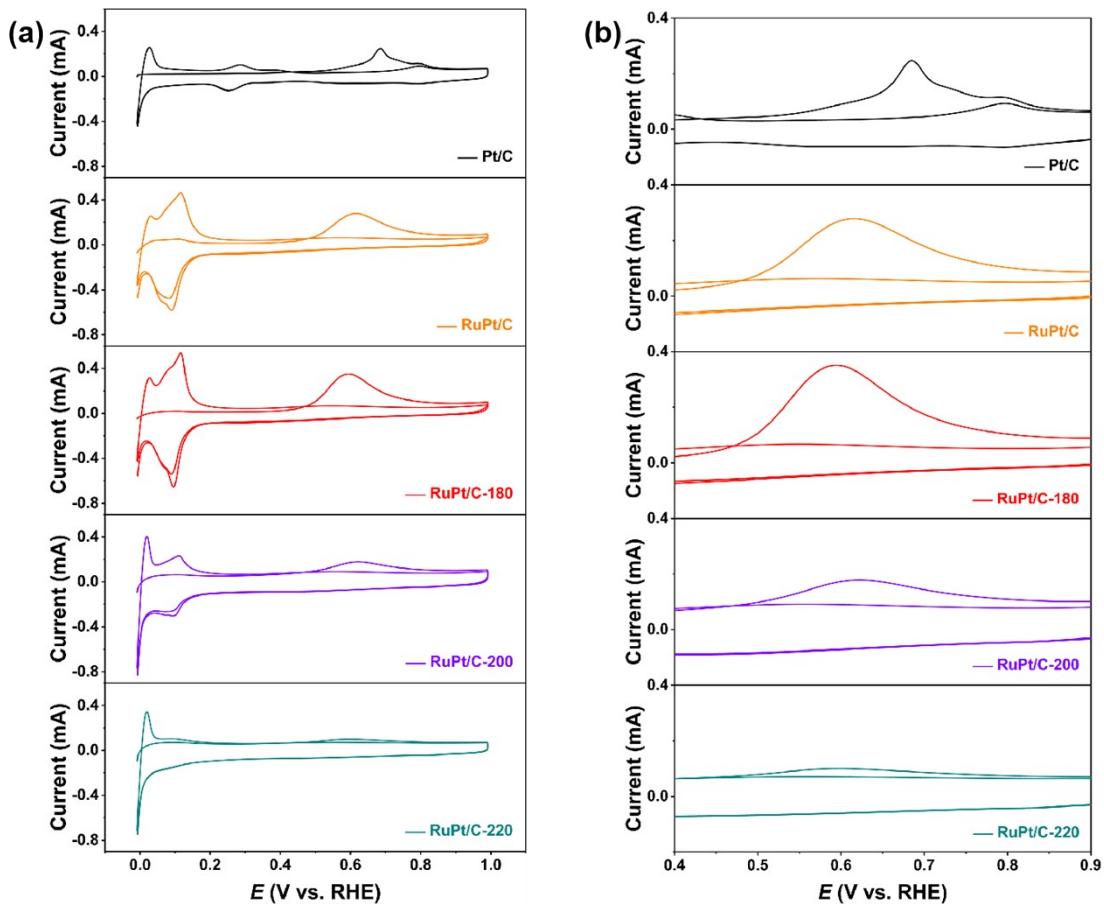
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191 **Fig. S10** High-resolution XPS spectra of (a) Pt 4f and (b) Ru 3p RuPt/C-200, RuPt/C-
192 200@CP before and after stability test.

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197 **Fig. S11** (a) original and (b) magnified CO-stripping voltammograms of commercial
 198 Pt/C, RuPt/C, RuPt/C-180, RuPt/C-200, and RuPt/C-220.

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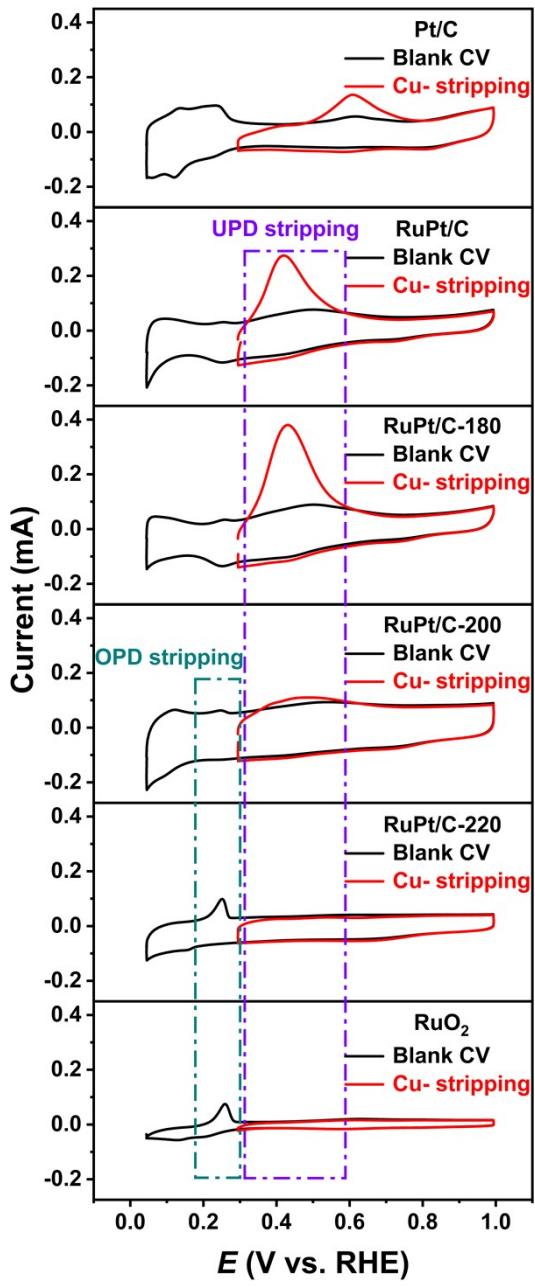
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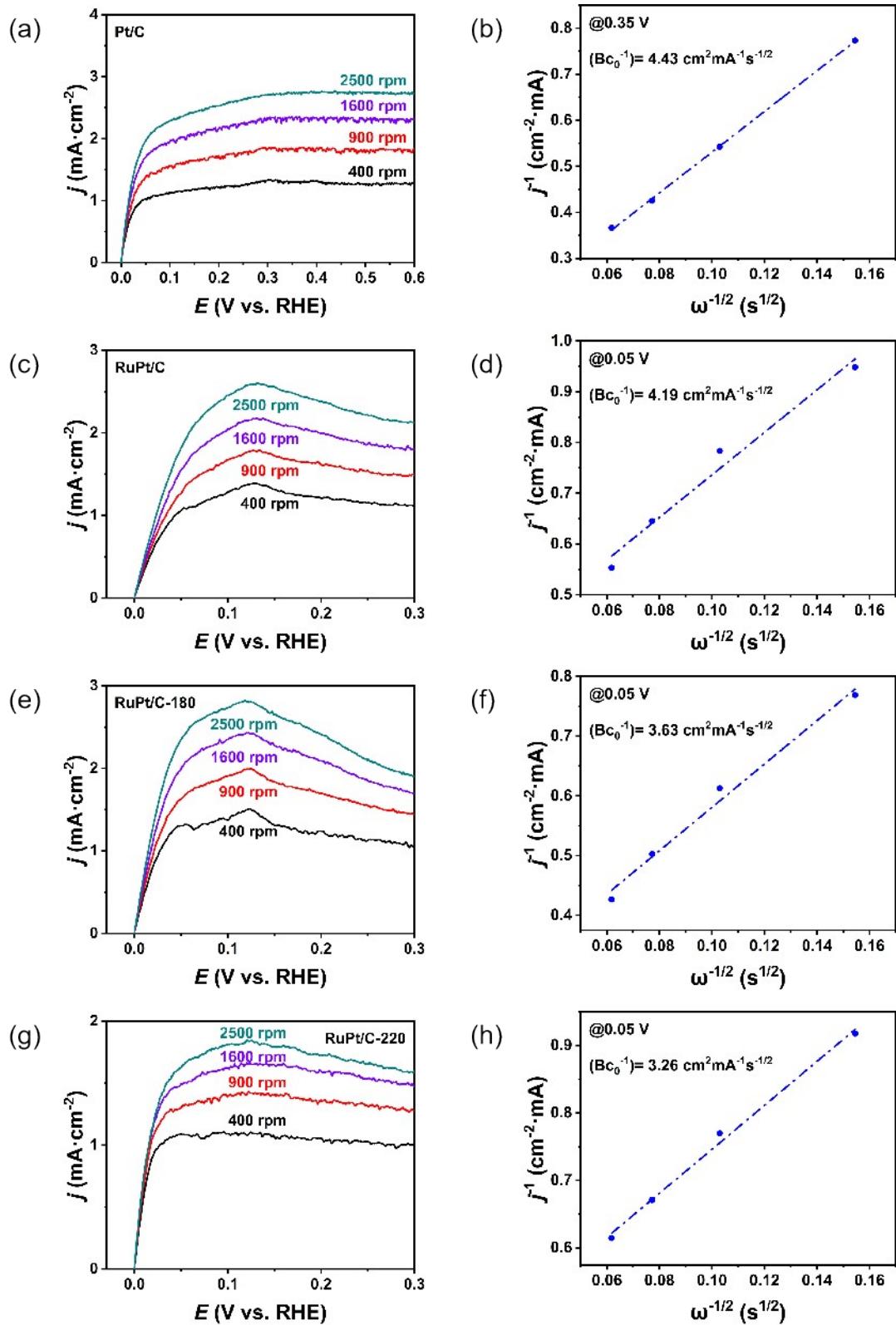
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220 **Fig. S12** CVs and Cu-stripping voltammograms of commercial Pt/C, RuPt/C,
 221 RuPt/C-180, RuPt/C-200, RuPt/C-220 and RuO₂ catalysts (loading amount: 122.4 ug cm⁻²).

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224 **Fig. S13** HOR polarization curves and corresponding Koutechy-Levich plots of (a, b)
225 Pt/C, (c, d) RuPt/C, (e,f) RuPt/C-180, and (g, h) RuPt/C-220 at different rotation
226 speeds in an H₂-saturated 0.1 M KOH solution with a scan rate of 5 mV s⁻¹. The BC₀

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{BC_0\omega^2}$$

values were derived from the Koutecky-Levich equation where ω is the rotation rate, and BC_0 is a constant related to the number of electrons transferred in a reaction, the gas concentration and diffusivity, and the electrolyte kinematic viscosity.

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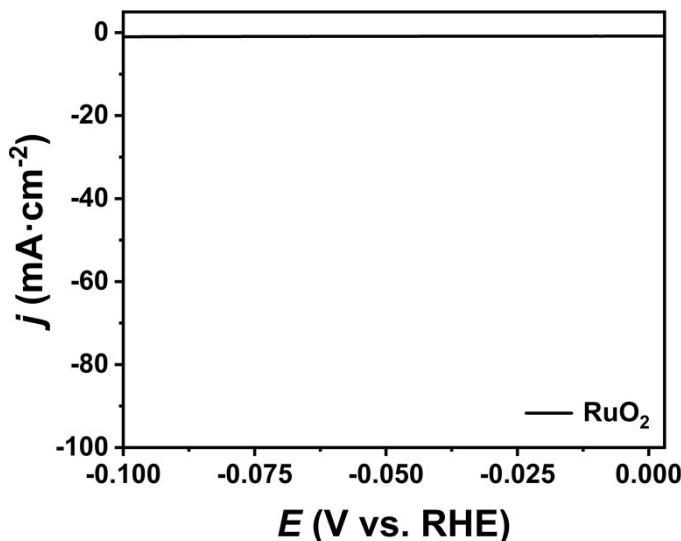
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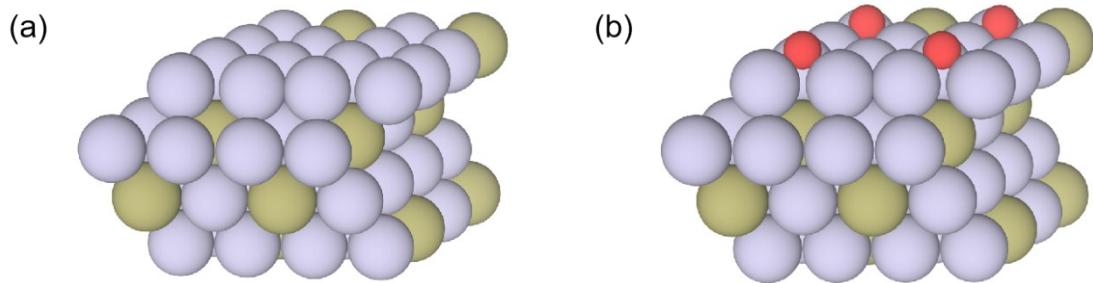
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262 **Fig. S14** HER polarization curves of commercial RuO₂ with 95% iR correction in a
263 N₂-saturated 1 M KOH electrolyte with a rotating speed of 1,600 rpm.
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294 **Fig. S15** The Optimized configurations of (a) pristine RuPt (111) surface and (b)
295 partially oxidized RuPt (111).

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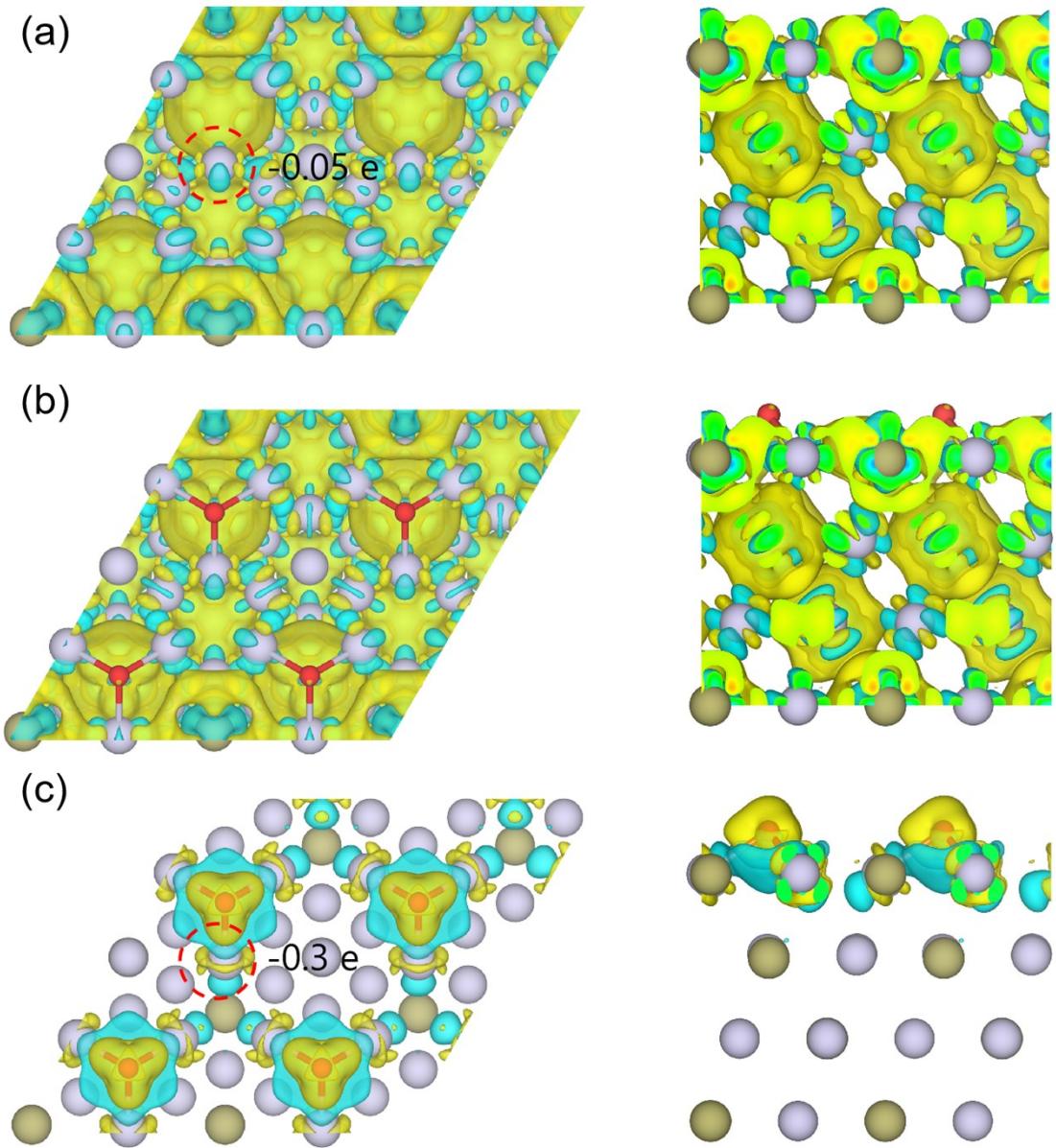
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 304 **Fig. S16** The top (left) and side (right) view of differential charge density between Pt
 305 and Ru for (a) RuPt ($\Delta\rho_1(\text{RuPt}) = \rho(\text{RuPt}) - \rho(\text{Ru}) - \rho(\text{Pt})$) and (b) oxidized RuPt
 306 ($\Delta\rho_2(\text{O-RuPt}) = \rho(\text{O-RuPt}) - \rho(\text{O-Ru}) - \rho(\text{Pt})$). (c) Differential charge density between
 307 O and Ru for oxidized RuPt ($\Delta\rho_3(\text{O-RuPt}) = \rho(\text{O-RuPt}) - \rho(\text{O}) - \rho(\text{RuPt})$). The value
 308 of isosurface is 0.004 eV A^{-3} . The cyan and yellow clouds represent electron depletion
 309 and accumulation, respectively. The values in the figure represent the number of loss
 310 electrons from Ru atoms.

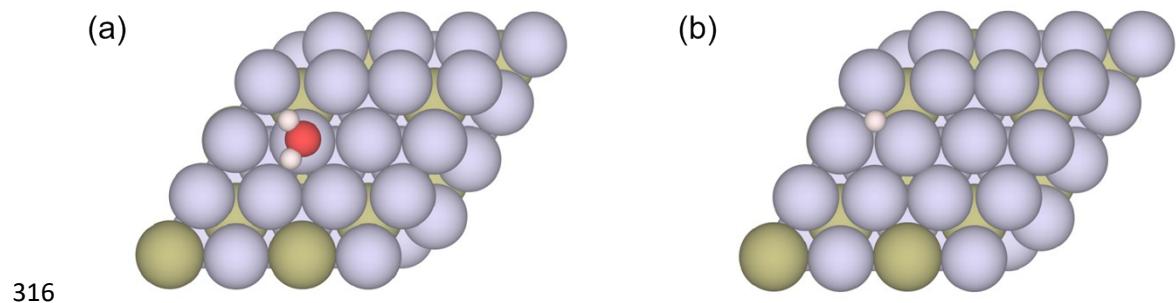
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317 **Fig. S17** Optimized atomic structure of RuPt with (a) H_2O adsorption, (b) $^*\text{H}$
318 adsorption on RuPt.

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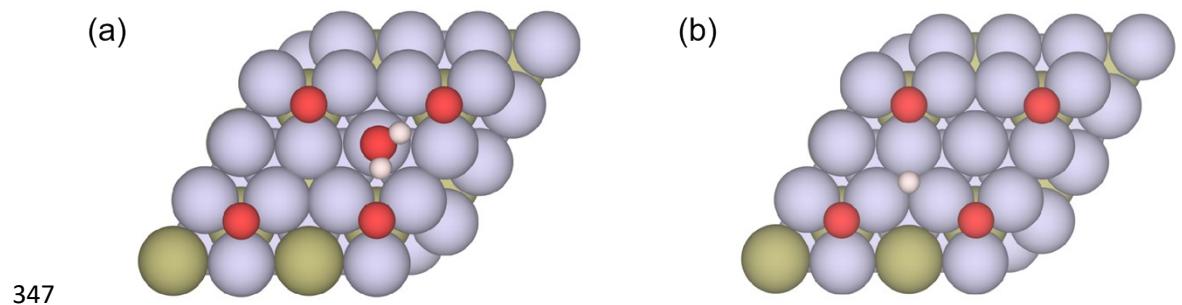
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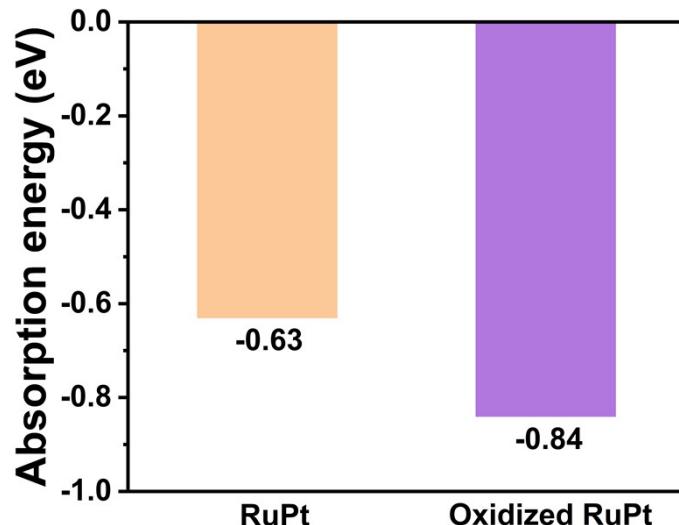
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348 **Fig. S18** Optimized atomic structure of (a) H_2O adsorption, (b) $^*\text{H}$ adsorption on
349 oxidized RuPt.

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373 **Fig. S19** Adsorption energies of water on pristine RuPt and oxidized RuPt.

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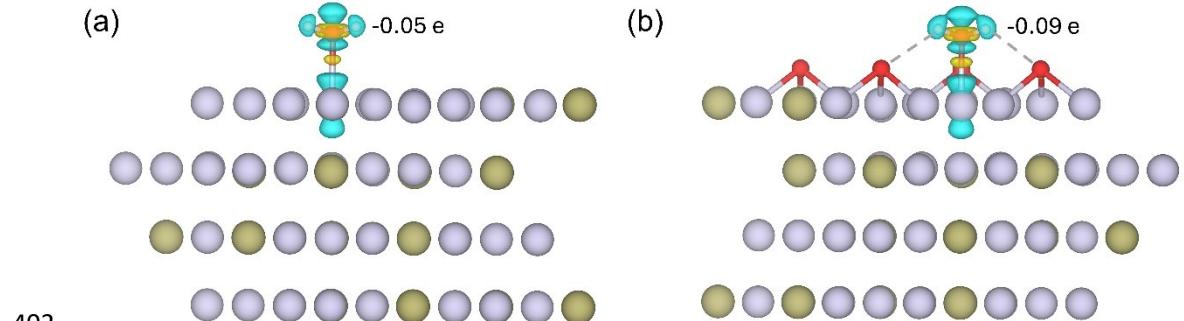
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403 **Fig. S20** Differential charge density between H_2O and (a) RuPt, (b) oxidized RuPt.
 404 The dotted line represents the hydrogen bond between H in H_2O and surface O. The
 405 value of isosurface is $0.004 \text{ eV } \text{\AA}^{-3}$. The cyan and yellow clouds represent electron
 406 depletion and accumulation, respectively. The values in the figure represent the
 407 number of donated electrons from H_2O .

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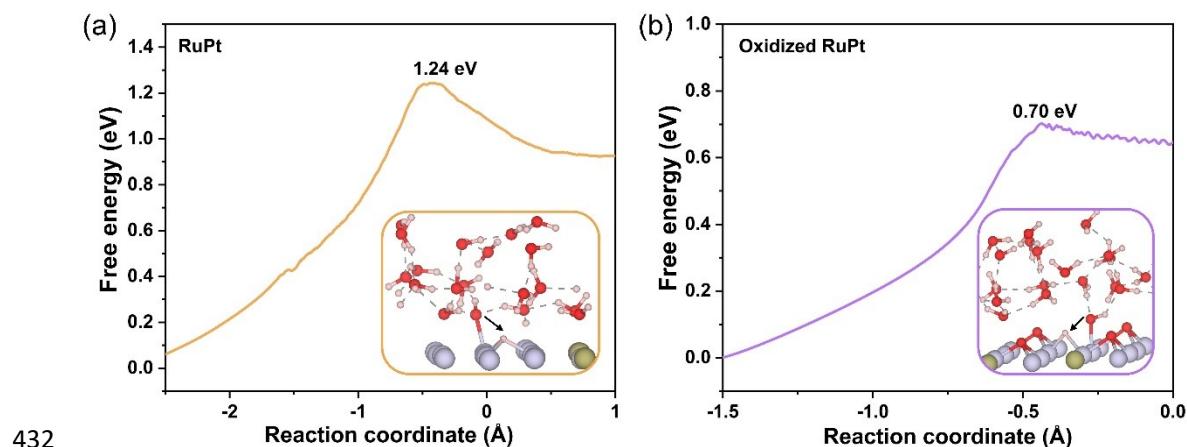
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433 **Fig. S21** The kinetic barrier for H_2O dissociation to ${}^*\text{H}$ and ${}^*\text{OH}$ on (a) RuPt and (b)
434 oxidized RuPt. The insets are the snapshots of the transition states.

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466 **Table S1.** The Pt/Ru molar ratio of the corresponding nanocrystals determined by
467 ICP-MS.

Samples	Pt (at.%)	Ru (at.%)
RuPt/C	20.81	79.19
RuPt/C-180	20.90	79.10
RuPt/C-200	20.94	79.06
RuPt/C-220	20.93	79.07
Ru ₈₄ Pt ₁₆ /C-200 (with less Pt)	16.28	83.72
Ru ₆₈ Pt ₃₂ /C-200 (with less Ru)	31.73	68.27

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490 **Table S2.** The values of $2\theta(^{\circ})$, lattice spacing (d) and derived lattice strain (s) of Pt
491 (111) (JCPDS no. 04-0802), RuPt/C, RuPt/C-180, RuPt/C-200 and RuPt/C-220.

Samples	$2\theta(^{\circ})$	d	s
Pt (111) (JCPDS no. 04-0802)	39.763	2.2650	0
RuPt/C	40.475	2.2268	1.69%
RuPt/C-180	40.435	2.2287	1.60%
RuPt/C-200	40.405	2.2305	1.52%
RuPt/C-220	40.427	2.2293	1.58%

492 According to a previous definition, the lattice strain of Pt (111) can be obtained by the
493 following equation¹:

$$494 s = \frac{d_n - d_b}{d_b} \times 100\%$$

495 Where d_b is the lattice spacing of bulk Pt (that is, 0.2265; JCPDS no. 04-0802), and d_n
496 is the lattice spacing of the corresponding RuPt nanocrystals. A positive value of
497 lattice strain (s) represents tensile strain, while a negative value represents
498 compressive strain.

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512 **Table S3.** The results of deconvolution of the Ru $3d_{3/2}$, Pt $4f$ and O $1s$ XPS spectra of
 513 different catalysts.

	Ru $3d_{5/2}$	Pt $4f$	O $1s$		
	BE/eV	Atomic Ratio (to Ru 0)	BE/eV	BE/eV	Area Ratio (to O $_L$)
RuPt/C	280.58	1	72.21	530.72 (O $_{Lat}$)	1
	281.15	1.35		532.84 (O V)	10
				534.28 (O $_{Abs}$)	5.8
RuPt/C-180	280.56	1	72.13	530.51 (O $_{Lat}$)	1
	281.31	1.34		532.89 (O V)	4.35
				534.32 (O $_{Abs}$)	2.09
RuPt/C-200	280.53	1	72.02	530.48 (O $_{Lat}$)	1
	281.21	2.14		532.79 (O V)	3.13
				534.25 (O $_{Abs}$)	1.41
RuPt/C-220	280.51	1	71.99	530.05 (O $_{Lat}$)	1
	281.35	5.80		532.80 (O V)	0.65
				534.46 (O $_{Abs}$)	4.35

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539 **Table S4.** Comparison of impedance of different catalysts.

Samples	R _s (ohm)	R _{ct} (ohm)
Pt/C	5.61	15.3
RuPt/C	5.65	6.79
RuPt/C-180	5.51	4.73
RuPt/C-200	5.59	1.57
RuPt/C-220	5.31	2.43

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576 **Table S5.** Comparison of overpotential at 10 mA cm⁻² and Tafel plots of different
 577 catalysts for alkaline HER in 1 M KOH electrolyte.

Catalysts	η_{10} (mV)	Tafel slope (mV dec ⁻¹)	Ref.
RuPt/C-200	4.4	18.4	This work
Ru-CrO_x@CN	7	30.1	²
Ru-Ga_{SA}/N-C	5	21.1	³
Ru@CQDs	10	47	⁴
Ru₂P/WO₃@NPC	15	18	⁵
RuMo₂C@CNT	15	26	⁶
Pt-Ru/RuO₂	18	18.5	⁷
2DPC-RuMo	18	25	⁸
D-NiO-Pt	20	31.1	⁹
Pt_{SA}-Mn₃O₄	24	54	¹⁰
2D-Pt ND/LDH	25	32.2	¹¹
Ru/np-MoS₂	30	31	¹²
CoPt-Pt_{SA}	31	43.65	¹³
Vo-Ru/HfO₂-OP	39	29	¹⁴
Ni₅P₄-Ru	54	52	¹⁵

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