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1 Ru-W Pair Sites Enabling the Ensemble Catalysis for Efficient Hydrogen Evolution

2

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38 Keywords: Ru-W pair site, optimizing elementary steps, Ru single-atom, efficient hydrogen
39 evolution

40

41 Simultaneously optimizing elementary steps such as water dissociation, hydroxyl transferring,
42 and hydrogen combination is crucial yet challenging for efficient hydrogen evolution reaction
43 (HER) in alkaline media. Herein, we developed Ru single atom-doped WO₂ nanoparticles
44 with atomically dispersed Ru-W pair sites (Ru-W/WO₂) through a crystalline lattice-confined
45 strategy for efficient alkaline HER. It was found that Ru-W/WO₂ exhibited remarkable HER
46 activity with a low potential (11 mV at 10 mA cm⁻²), notable mass activity (5863 mA mg⁻¹Ru
47 at 50 mV), as well as robust stability (500 h at 250 mA cm⁻²). The highly efficient activity of
48 Ru-W/WO₂ stem from the synergistic effect of Ru-W sites through ensemble catalysis, in
49 which the W sites expedite rapid hydroxy transferring and water dissociation, and the Ru sites
50 accelerate the hydrogen combination process, synergistically facilitating the HER activity.
51 This study opens a promising pathway for tailoring the coordination environment of atomic-
52 scale catalysts to achieve efficient electrocatalysis.

53

54 **1. Introduction**

55 Water electrolysis powered by sustainable electricity offers a cost-effective and readily
56 available approach for producing green hydrogen, and is considered a key element in
57 achieving future carbon neutrality.^[1-3] The hydrogen evolution reaction (HER) plays a pivotal
58 role in water electrolysis, but the use of noble-based anode catalysts and expensive proton
59 exchange membranes in acidic electrolytes has prompted the search for efficient alkaline HER
60 electrocatalysts.^[4-5] Recently, platinum (Pt) based materials are considered the benchmark and
61 most capable electrocatalysts for HER, but their scarcity poses significant limitations for
62 practical applications,^[6] Ruthenium (Ru) as one of the platinum-group metals is identifying as
63 an ideal alternative for developing efficient HER catalysts.^[7] However, the strong interaction
64 of hydrogen and hydroxyl species over Ru species hinders further water dissociation,
65 hydrogen desorption, and combination processes, resulting in unsatisfactory HER
66 performance.^[8] Therefore, there is a pressing need to selectively tailor the electronic structure
67 of Ru to fine-tune the adsorption and desorption abilities of hydrogen and hydroxyl species in
68 a controlled manner, but still challenging.

69 Single atom catalysts (SACs) with tunable local coordination environment represent a
70 promising material platform for modulating the electronic structures of active sites,^[9,10] as
71 demonstrated by their ability to optimize the free energy of intermediates during the HER
72 process.^[11] Currently, various Ru SACs have been developed by modulating anions ligands in
73 the first coordination shell, resulting in excellent alkaline HER activity, such as Ru
74 SAs@PN,^[12] Ru-MoS₂/CC,^[13] R-NiRu,^[14] RuSA-Ti₃C₂T_x,^[15] etc. In these cases, the anions
75 ligands surrounding the Ru site regulate the strong adsorption of hydrogen on Ru, promoting
76 H desorption and combination. However, these isolated Ru sites still exhibit strong hydroxyl
77 adsorption,^[8,16] as the single active sites are unable to break the scaling relation.^[17,18] Recently,
78 tailoring the coordination fields through cation regulation has been shown to efficiently
79 improve catalytic activity, particularly for complex multistep reactions.^[19,20] Electro-catalysts

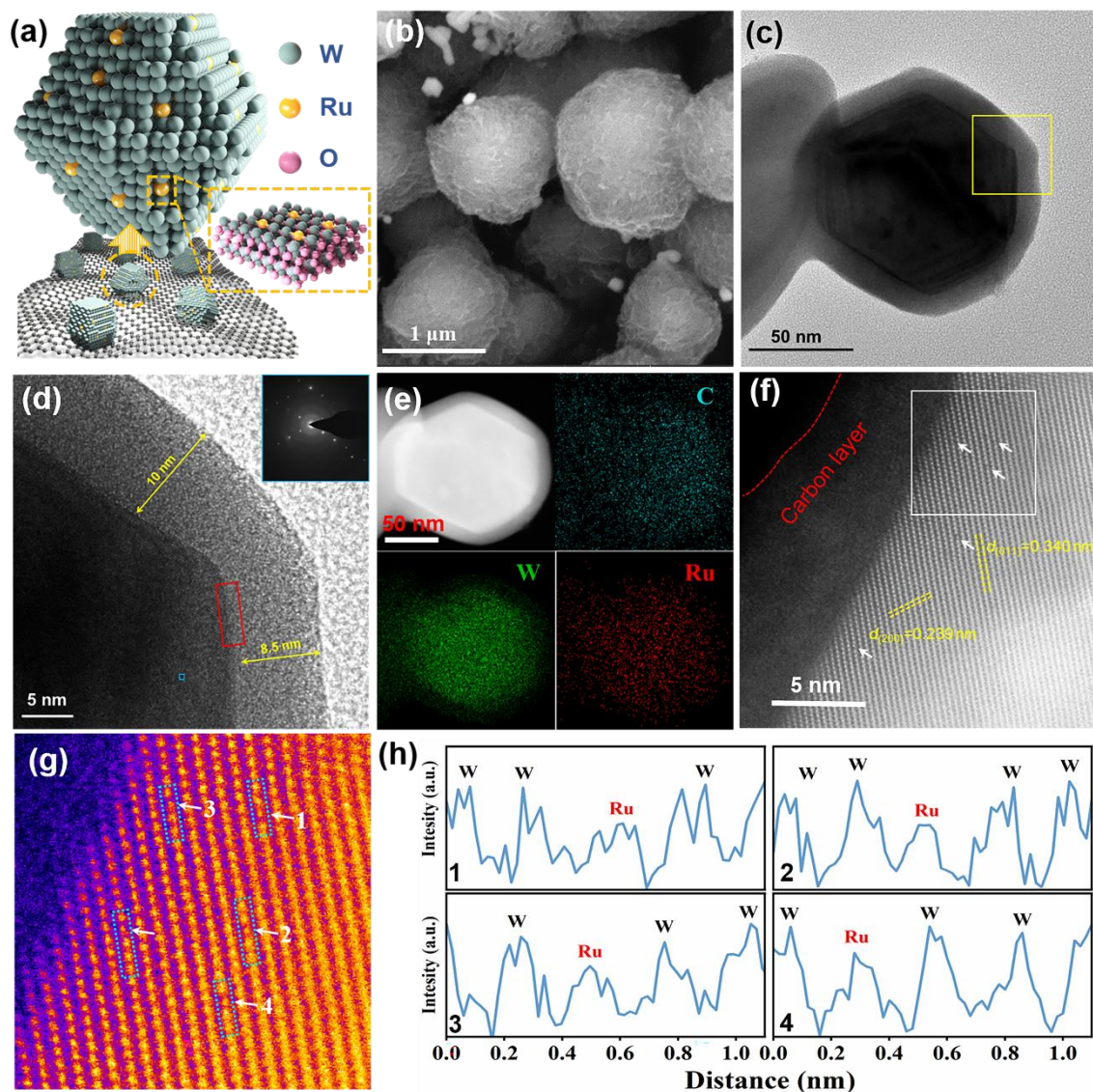
80 containing paired metal sites offer significant potential to precisely design the active moiety
81 for regulating the binding energy of multiple intermediates simultaneously,^[21-22] which is
82 advantageous for alkaline HER but has been rarely investigated.

83 Inspired by the pioneering works exploiting W as regulator for Ru nanoparticles,^[23-26] we
84 employ a lattice-confined strategy to construct Ru-W/WO₂-800 catalysts with well-defined
85 Ru-W pair sites through cation replacement. XAFS and STEM analyses confirm that Ru
86 atoms are embedded into the crystalline lattice of WO₂ and strongly bonded with adjacent W
87 atoms. The optimized catalyst exhibits remarkable activity for HER in alkaline media, with a
88 low overpotential of only 11 mV at 10 mA cm⁻², high mass activity of 3829 mA mg⁻¹Ru at 50
89 mV, and robust stability up to 500 hours at 250 mA cm⁻². Operando electrochemical Raman
90 measurements, combined with theoretical calculation, reveal that the superior activity of Ru-
91 W/WO₂-800 derive from the synergistic effect of Ru-W pair sites through ensemble catalysis.
92 Specifically, the W sites facilitate rapid hydroxyl transfer and water dissociation, while the Ru
93 sites accelerate the hydrogen combination process, synergistically enhancing the HER activity.

94 **2. Results and Discussion**

95 **2.1. Ru-W pair catalysts synthesis.**

96 Figure S1 (Supporting Information) illustrate the synthetic process of the Ru-W pair
97 doped WO₂. Typically, dopamine hydrochloride is firstly mixed with RuCl₃ in acidic solution,
98 then Na₂WO₄ is added to gain spherical polydopamine-based metal-organic compounds
99 (Figure S2 and S3, Supporting Information). After annealing in inert atmosphere at 800 °C,
100 Ru-W/WO₂-800 with Ru-W dual sites on tungsten oxide is obtained (Figure 1a). In order to
101 investigate the pivotal role of the Ru-W pair in Ru-W/WO₂-800, single atom Ru supported on
102 WO₂ (Ru₁/WO₂-800) is prepared as comparison (Figure S4, Supporting Information).
103 Furthermore, nitrogen-coordinated single atom Ru (Ru SACs, Figure S5, Supporting
104 Information), commercial Ru/C, commercial Pt/C and tungsten oxide (WO₂-800, Figure S6,
105 Supporting Information) are also used as references.



106

107 **Figure 1.** (a) Simulative structure and (b) SEM image of Ru-W/WO₂-800. (c, d) TEM images
 108 and (e) EDS element mapping of a well-crystallized WO₂ in Ru-W/WO₂-800. (f, g) HAADF-
 109 STEM images of the atom arrays of the WO₂ crystal and the surface Ru-W atom pairs. (h)
 110 Line intensity profiles along the (011) plane in g.

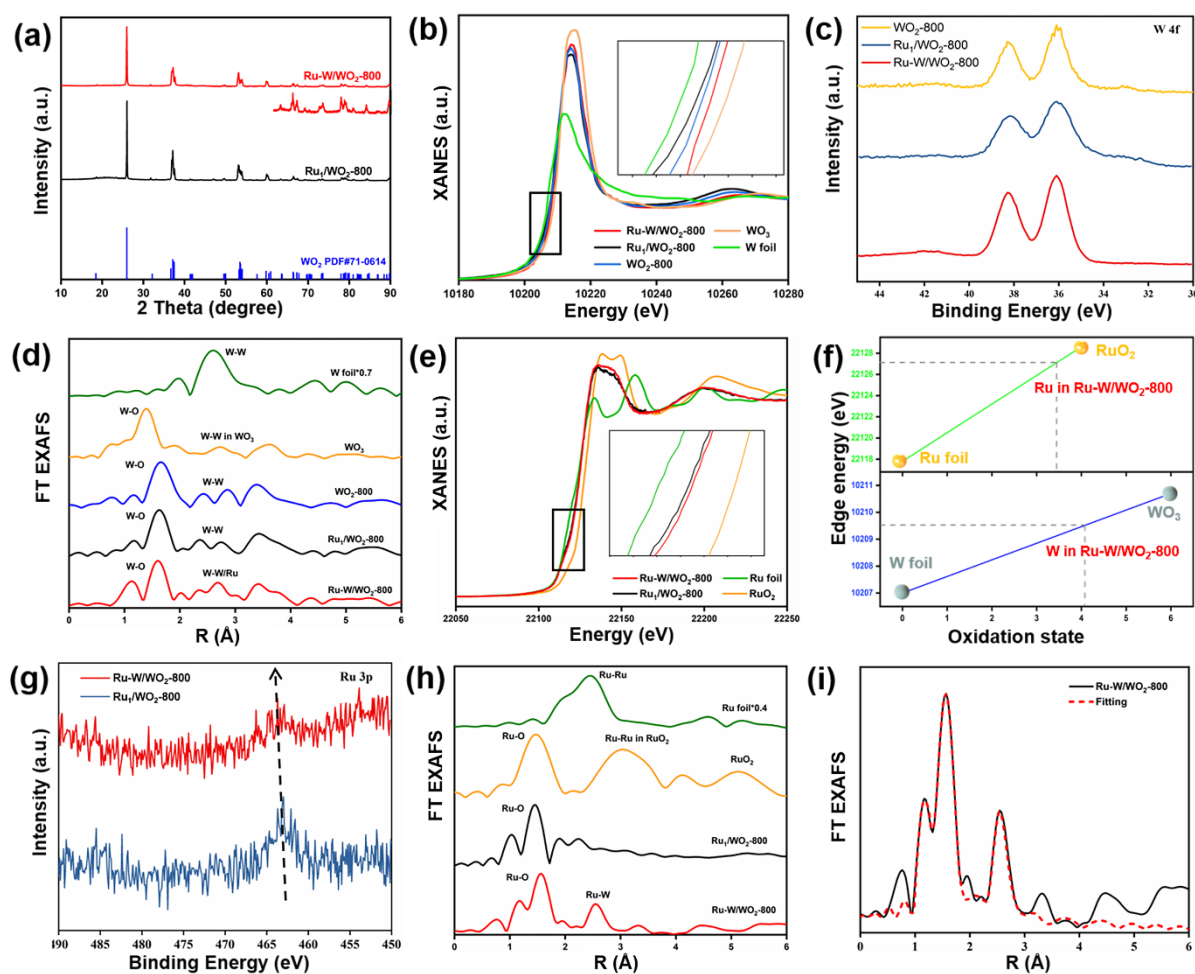
111 2.2. Physical characterization.

112 The element mapping results of Ru-W/WO₂-800 indicate the existence and the uniform
 113 distribution of W and Ru over carbon substrate (Figure S7, Supporting Information). The
 114 corresponding W and Ru contents are confirmed as 25 wt% and 1.3 wt% by ICP (Table S1,
 115 Supporting Information), respectively. Figure 1b displays the SEM images of Ru-W/WO₂-800,
 116 which reveals a spherical morphology consisted by the aggregation of nano flakes. The TEM
 117 image further confirms the randomly dispersion of WO₂ particles and nano clusters in the

118 agminated flakes (Figure S8, Supporting Information). Considering the insufficient ability of
119 single atom Ru or W doped carbon in HER,^[26,27] the potential active sites for HER are
120 mainly concentrate on the well-crystallized WO₂ particles in Ru-W/WO₂-800. As shown in
121 Figure 1c, the WO₂ crystal takes a hexagonal morphology, a carbon layer about 8-10 nm is
122 observed enveloping the WO₂ (Figure 1d), which may help promoting its stability. The EDS
123 element mapping confirms the carbon enveloping and the uniform distribution of Ru on WO₂
124 particle (Figure 1e). The aberration-corrected HAADF-STEM is employed to study the surface
125 structure of the WO₂ particle. As shown in Figure 1f, W atomic array with lattice spacing of
126 0.239 and 0.340 nm are clearly observed, which correspond to the (200) and (011) plane of
127 the monoclinic WO₂. Moreover, some dark atomic columns are observed inserting in the W
128 atomic array randomly, which could be distinguished as Ru atom on the surface of WO₂
129 (Figure 1g). Line profiles of the HAADF-STEM are taken around Ru atom along the (011)
130 plane, the variable atomic column intensity in Figure 1h demonstrating the replacement of
131 lattice W atom by Ru atom. Moreover, the Ru sites doping in WO₂ lattice are also
132 distinguished on the WO₂ clusters in Ru-W/WO₂-800 (Figure S9, Supporting Information).
133 For Ru₁/WO₂-800, the HAADF-STEM image reveals the WO₂ atom array and dark atomic
134 columns of Ru (Figure S10, Supporting Information), and the distortion of atom array around
135 Ru atom. However, whether the Ru in Ru₁/WO₂-800 and Ru-W/WO₂-800 manifest as Ru
136 single atom or Ru-W coordination still need be further distinguished by spectral investigations.

137 Figure 2a show the XRD pattern of Ru doped WO₂ catalysts, both Ru-W/WO₂-800 and
138 Ru₁/WO₂-800 display the diffraction peaks belonging to (011), (200), (-202), (-220) and (310)
139 planes of monoclinic WO₂ at 25.9°, 36.7°, 37.5°, 53.3° and 60.0°, and the peaks of crystalline
140 Ru is absent. To further distinguish the Ru and W combination in Ru-W/WO₂-800 and
141 Ru₁/WO₂-800, the X-ray adsorption fine spectroscopy (XAFS) are exploited. The oxidation
142 state of W in Ru-W/WO₂-800, Ru₁/WO₂-800 and WO₂-800 are confirmed similar based on

143 the W L_3 -edge XANES spectra (Figure 2b), which approximate to +4, consisting with the W
 144 4f



145
 146 **Figure 2.** Coordination environment of Ru-W/ WO_2 -800 and Ru_1/WO_2 -800. (a) XRD patterns.
 147 (b) W L_3 -edge XANES spectra. (c) W 4f XPS spectra. (d) W L_3 -edge edge FT EXAFS spectra.
 148 (e) Ru K -edge XANES spectra. (f) The simulative oxidation state of Ru and W in Ru-
 149 W/ WO_2 -800. (g) Ru 3p XPS spectra. (h) Ru K -edge FT EXAFS spectra. (i) FT EXAFS fitting
 150 curve of Ru-W/ WO_2 -800 at R space.

151 XPS spectra (Figure 2c).^[28] The W L_3 -edge FT EXAFS spectra are shown in Figure 2d, the
 152 differences of the secondary coordination between Ru-W/ WO_2 -800, Ru_1/WO_2 -800 and WO_2 -
 153 800 suggesting the disturbance of W-W coordination in Ru-W/ WO_2 -800 induced by the Ru
 154 inserting. To further reveal the interaction of the Ru-W pair in Ru-W/ WO_2 -800, the Ru K -
 155 edge XAS are taken in reference to Ru_1/WO_2 -800, Ru foil and RuO_2 . Figure 2e shows the Ru
 156 K -edge XANES. According to the location of white-line intensity of Ru-W/ WO_2 -800, which
 157 between that of Ru foil and RuO_2 , the oxidative state of Ru in Ru-W/ WO_2 -800 is indicated

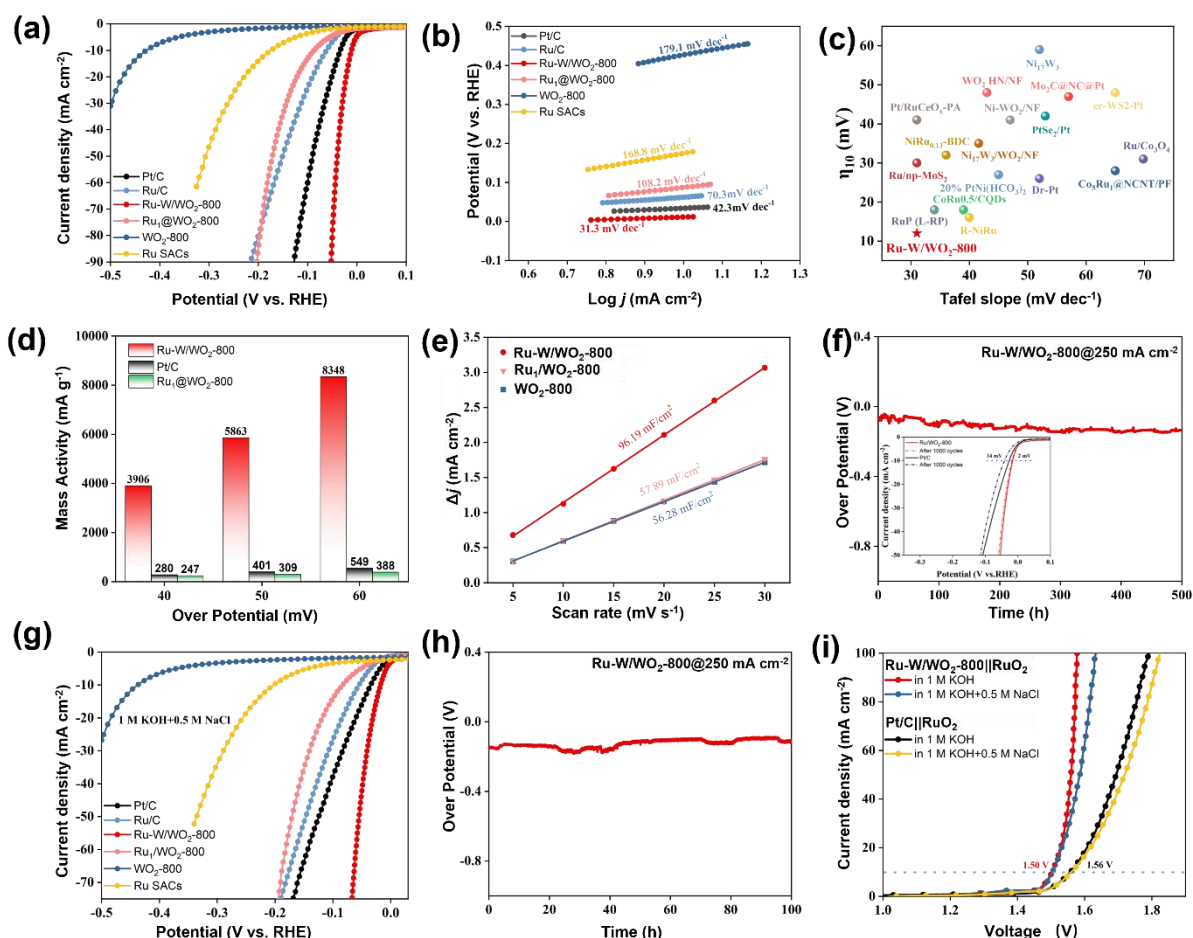
158 between 0 and +4. The linear simulation of edge energy and oxidation state is practiced in
159 Figure 2f. The fitting result discloses that the average oxidation state of Ru in Ru-W/WO₂-800
160 is +3.4, slightly higher than the +3.3 in Ru₁/WO₂-800 (Figure S11, Supporting Information),
161 in line with the Ru 3p XPS spectra (Figure 2g).^[29] The Ru K-edge FT EXAFAS of Ru-
162 W/WO₂-800 displays a dominant peak at ~1.5 Å (Figure 2h), which belonging to the Ru-O
163 coordination. Moreover, the secondary peak at ~2.5 Å demonstrates the existence Ru-W
164 coordination, which is larger than the Ru-Ru bonding in Ru foil (~2.4 Å), due to relatively
165 bigger atomic diameter of W. Figure 2i and Table S2(Supporting Information) give the Ru K-
166 edge EXAFS fitting results of Ru-W/WO₂-800. The coordination number of Ru-O bonding
167 and Ru-W bonding are simulated as 3.1 and 0.9, respectively, indicating the formation of Ru-
168 W dual atom sites, which embedding into the lattice of WO₂ crystalline. For Ru₁/WO₂-800,
169 only a dominant peak at ~1.5 Å is observed in the Ru K-edge EXAFS, the absence of Ru-Ru
170 and Ru-W coordination confirm the Ru single atom are absorbed onto the surface of WO₂.

171

172 **2.3. Electrocatalytic performance evaluation.**

173 The synergistic effect of the Ru-W bonding should be benefit for the boosting of the
174 hydrogen evolution process. Thus, we employ the three-electrode system to evaluate the HER
175 performance of Ru-W/WO₂-800, in reference to Ru₁/WO₂-800, WO₂-800, Ru SACs,
176 commercial Ru/C and Pt/C. Figure 3a show the linear sweep voltammetry (LSV) curves in 1
177 M KOH, in which the Ru-W/WO₂-800 displays a remarkable onset potential that near zero. A
178 significant reduced overpotential of 11 mV (at 10 mA cm⁻²) is confirmed over Ru-W/WO₂-
179 800 (Figure S12, Supporting Information), lower than that over Pt/C, Ru/C, Ru₁/WO₂-800, Ru
180 SACs and WO₂-800, demonstrating its superior HER performance. Moreover, Ru-W/WO₂-
181 800 also reveals a low potential of 152 mV to gain a current density of 1 A cm⁻² (Figure S13).
182 The insufficient activity of WO₂-800 indicates the dominant of Ru in actuating the HER

183 process. Furthermore, the relatively higher overpotential of Ru₁/WO₂-800 compared to that of
 184 Ru-W/WO₂-800 reveal the pivotal role of Ru-W bonding for boosting the HER pathway.



185
 186 **Figure 3.** HER evaluation in alkaline medium. (a) Linear sweep voltammetry (LSV) curves
 187 and (b) Tafel plots of Ru-W/WO₂-800 and reference catalysts. (c) Comparison of the HER
 188 performance between Ru-W/WO₂-800 and other reported catalysts. (d) Mass activity of Ru-
 189 W/WO₂-800, Ru₁/WO₂-800 and Pt/C. (e) The current density differences vs. scan rate and the
 190 corresponding yielded C_{dl} for Ru-W/WO₂-800, Ru₁/WO₂-800 and WO₂-800. (f)
 191 Chronopotentiometry test at 250 mA cm⁻² and the LSV curve of Ru-W/WO₂-800 before and
 192 after 1000 cycles (insert) in 1 M KOH. (g) LSV curves in alkaline simulated seawater of 1 M
 193 KOH and 0.5 M NaCl. (h) Chronopotentiometry test at 250 mA cm⁻² of Ru-W/WO₂-800 in
 194 alkaline simulated seawater. (i) Overall water-splitting performance of the Ru-W/WO₂-
 195 800||RuO₂ and Pt/C||RuO₂ electrode couples.

196 The much lower Tafel slope of Ru-W/WO₂-800 (31.3 mV dec⁻¹) further demonstrate its
 197 outstanding HER activity (Figure 3b), even compared with the previously reported works
 198 (Figure 3c). This observation can be attributed to the high intrinsic HER activity of Ru-
 199 W/WO₂-800, which is further confirmed by its notably turnover frequency (Figure S14,

200 Supporting Information). Figure 3d show the normalized activity based on the mass of metal,
201 Ru-W/WO₂-800 exhibits a mass activity of 5863 mA mg⁻¹Ru at 50 mV, over 14 times higher
202 than that of Pt/C (401 mA mg⁻¹Pt), suggesting its larger application potential. The larger
203 double-layer capacitances (C_{dl}) of Ru-W/WO₂-800 than that of Ru₁/WO₂-800 (Figure 3e and
204 Figure S15, Supporting Information), combining with the smaller charge transfer resistance
205 (Figure S16, Supporting Information), further demonstrating the evident advantage of the
206 synergistic Ru-W pair sites. Figure 3f present the stability tests. The robustness of Ru-
207 W/WO₂-800 is confirmed by the negligible increasing of the overpotential after 1000 cycles
208 and the superior long-term stability of Ru-W/WO₂-800 up to 500 h at 250 mA cm⁻².
209 Furthermore, the used Ru-W/WO₂-800 maintained its original structure, revealing the good
210 structure stability (Figure S17, Supporting Information).

211 Electrochemical hydrogen production exploiting seawater is drawing great attention
212 recently, due to the huge reserves of the feedstock.^[30,31] Thus, the hydrogen generation ability
213 of electrocatalysts in alkaline simulated seawater (1 M KOH and 0.5 M NaCl) are tested. As
214 shown in Figure 3g and Figure S18 (Supporting Information), although all catalysts display a
215 decline in the HER activity compared with that in alkaline fresh water, the Ru-W/WO₂-800
216 still exhibit a sufficient overpotential of 22 mV at 10 mA cm⁻² and a Tafel slope of 33.8 mV
217 dec⁻¹. The robustness of the Ru-W/WO₂-800 in alkaline simulated seawater is also confirmed
218 by the chronopotentiometry test at 250 mA cm⁻² up to 100 h (Figure 3h). Inspiring by the
219 excellent HER performance of Ru-W/WO₂-800 in both alkaline freshwater and alkaline
220 simulated seawater, the overall water-splitting is measured due to its significant
221 application.^[32-35] The electrolyzer is assembled by using Ru-W/WO₂-800 as cathode and
222 commercial RuO₂ as anode (Ru-W/WO₂-800 || RuO₂ couple), and in reference to Pt/C || RuO₂
223 couple. As shown in Figure 3i, the Ru-W/WO₂-800 || RuO₂ couple just require 1.50 mV to
224 gain a current density of 10 mA cm⁻² in 1 M KOH, lower than the 1.56 mV of Pt/C || RuO₂
225 couple. Moreover, the current density over Ru-W/WO₂-800 || RuO₂ couple was much higher

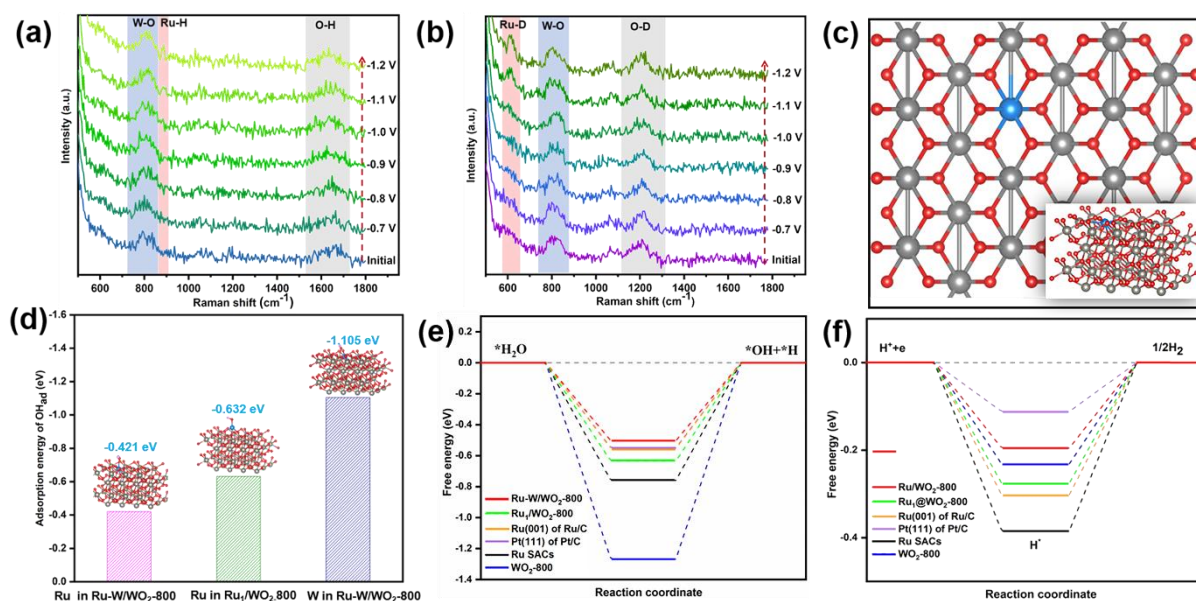
226 compare with that over Pt/C || RuO₂ couple at large voltages. The water-splitting ability of
227 Ru-W/WO₂-800 in seawater is also evaluated, in agreement with the LSV curve in Figure 3g,
228 a slight decline of the activity is observed due to the obstruction of active sites by the NaCl,
229 but its current density is still higher than that of Pt/C. The water splitting performance
230 demonstrate the application potential of Ru-W/WO₂-800 as cathode material for producing
231 green hydrogen by water electrolysis.

232 **2.4. Understanding the active sites.**

233 To clarify the HRE process, potential dependent operando Raman spectroscopy are
234 conducted in both H₂O and D₂O solution of 1 M KOH. The operando Raman spectra of Ru-
235 W/WO₂-800 are recorded at the potential from -0.7 to -1.2 V (vs. Ag/AgCl), which shifts
236 from the non-Faradaic region to the HER region. Figure 4a shows the Raman spectra of Ru-
237 W/WO₂-800 in the 1 M KOH solution of H₂O. The signal at 798 cm⁻¹ and 1634 cm⁻¹ should
238 belong to the W-O in WO₂ and H-O-H bending mode of water.^[36-38] Moreover, a new signal
239 emerges at 884 cm⁻¹ when negative shift the potential to -1.0 (vs. Ag/AgCl), the intensity of
240 which increases after further shift the potential to 1.2 (vs. Ag/AgCl). As reported, this signal
241 may be attributed to the Ru-H stretch.^[23] To clarify the attribution of the Raman signal at 884
242 cm⁻¹, 1 M KOH solution of D₂O is used. As shown in Figure 4b, after H₂O is changed to D₂O,
243 the signal at 884 cm⁻¹ shifts to 614 cm⁻¹, the downward shift ratio is estimated as 69.5%, close
244 to the theoretical 71.1%, which confirm the Ru-H stretch on Ru-W/WO₂-800. Considering the
245 Ru-H stretch emerges at a potential as low as -1.0 (vs. Ag/AgCl), efficient water dissociation
246 is demonstrated for Ru-W/WO₂-800.

247 DFT calculations are used to further dig the original effect of the Ru-W synergy on the
248 HER pathway. A model with bonded Ru-W pair in cell of WO₂ is constructed based on the
249 experimental results of Ru-W/WO₂-800 (Figure 4c). For comparison, the model of Ru
250 adsorbed on the surface of WO₂ (Ru₁/WO₂-800), pure WO₂ (WO₂-800) and N-coordinated Ru
251 single atom (Ru SACs) are also built (Figure S19, Supporting Information). The OH_{ad}

252 poisoning effect is firstly investigated by the absorption energy of OH_{ad} ($E_{\text{abs}}\text{OH}$). As shown
 253 in Figure 4d and Figure S20 (Supporting Information), the Ru site in Ru-W/ WO_2 -800 exhibits
 254 a $E_{\text{abs}}\text{OH}$ of -0.421 eV, higher than that of Ru site in Ru_1/WO_2 -800 (-0.632 eV) and Ru site in
 255 Ru SACs (-0.632 eV), suggesting the weakening of Ru-OH interaction by Ru-W pair.
 256 Moreover, the strong interactions of W-OH on W site in Ru-W/ WO_2 -800 and W site in WO_2 -
 257 800 further demonstrate the optimizing of the OH absorption over Ru-W dual atom sites in
 258 Ru-W/ WO_2 -800.



259
 260 **Figure 4.** (a, b) Operando Raman spectra of Ru-W/ WO_2 -800 at different potential vs.
 261 Ag/AgCl in 1 M KOH in H_2O (a) and D_2O (b). (c) Simulative structure of Ru-W/ WO_2 -800.
 262 (d) Simulative OH adsorption model and corresponding adsorption energy on Ru and W sites.
 263 (e) Free energy diagram for water dissociation. (f) Free energy diagram for hydrogen
 264 recombination.

265
 266 Figure S21 (Supporting Information) presents the absorption energy of H_2O ($E_{\text{abs}}\text{H}_2\text{O}$),
 267 which disclosed the faster H_2O capture on the Ru site in Ru-W/ WO_2 -800 ($E_{\text{abs}}\text{H}_2\text{O}=-1.325$
 268 mV) compared with that on Ru_1/WO_2 -800 and Ru SACs, suggesting the acceleration of the
 269 following H_2O dissociation step. The optimal water dissociation intermediate (H-OH) on Ru-
 270 W/ WO_2 -800 is demonstrated in Figure S22 (Supporting Information) as the $^*\text{H}$ absorbing on
 271 Ru site and $^*\text{OH}$ absorbing on the bonded W site. Based on this optimal structure, Ru-
 272 W/ WO_2 -800 displays the lowest H_2O dissociation barrier of 0.50 eV compared with Ru single

273 atom, Pt/C and Ru/C (Figure 4e), indicating its best H₂O dissociation ability. Furthermore, the
274 optimized the hydrogen recombination ability of Ru-W/WO₂-800 in alkaline medium is also
275 revealed by the DFT calculations (Figure 4f and Figure S23, Supporting Information). Overall,
276 compared with the adsorbed Ru on WO₂ in Ru₁/WO₂-800, the bonded Ru-W dual atom site in
277 the WO₂ lattice gives Ru-W/WO₂-800 the solid advantages of: (1) rapid hydroxy transferring
278 performance, (2) superior H₂O dissociation ability, (3) optimized the hydrogen recombination.
279 Thus, the HER performance of Ru/WO₂-800 in alkaline medium is significant boosted by the
280 synergistic effect of the Ru-W dual atom sites.

281 **3. Conclusion**

282 In this work, we fabricated a Ru single atom doped WO₂ by lattice confined strategy,
283 which was identified as bonded Ru-W pairs embedding in the lattice of well-crystallized WO₂.
284 The resultant Ru-W/WO₂-800 delivered excellent HER performance under alkaline and
285 seawater media with ultralow overpotential and remarkable mass activity, as well as robust
286 stability at high current density. Moreover, the Ru-W/WO₂-800 also presented low voltages in
287 overall water splitting system, beneficial for practical application. The DFT calculation
288 combining with the operando Raman spectra revealed that the outstanding HER activity stems
289 from the synergetic effect of Ru-W pair sites via an ensemble catalysis, in which the W sites
290 expedite the rapid hydroxy transferring and water dissociation, the Ru sites accelerate the
291 hydrogen combination process. This work may provide important inspire for designing
292 atomic-scale catalysts aiming at complicated electrocatalysis.

293

294 **Supporting Information**

295 Supporting Information is available from the Wiley Online Library or from the author.

296

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303

304 **Conflict of Interest**

305 The authors declare no Conflict of Interest.

306

307 **Author contributions**

308 K.L. and Y.Q. designed and wrote this work. J.B. and X.L. supervised and funded this work.

309 W.M. conducted the catalysts synthesis and the HER evolutions. X.Y., D.L., R.X., L.N. and

310 L.Z. gave their helps in the characterizations. P.B. and S.W designed and practiced the

311 operando Raman measurements. Y.W., G.W. and J.D. co-modified the paper. All authors

312 revised the writing work of this study.

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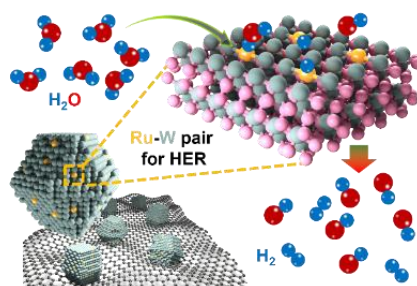
401 Atomically dispersed Ru-W pair site doping WO₂ are fabricated as alternative of Pt-based
402 materials for developing efficient alkaline HER catalyst. The synergistic effect of Ru-W sites
403 triggers ensemble catalysis, resulting in superior performance for electrochemical hydrogen
404 generation.

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406 *Weilong Ma, Xiaoyu Yang, Dingding Li, Ruixin Xu, Liangpeng Nie, Baoping Zhang, Yi Wang,*
407 *Shuang Wang, Gang Wang, Jinxiang Diao, Lirong Zheng, Jinbo Bai, Kunyue Leng*, Xiaolin*
408 *Li* and Yunteng Qu**

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410 **Ru-W Pair Sites Enabling the Ensemble Catalysis for Efficient Hydrogen Evolution**

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415 Supporting Information

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418 **Ru-W Pair Sites Enabling the Ensemble Catalysis for Efficient Hydrogen Evolution**

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420 *Weilong Ma, Xiaoyu Yang, Dingding Li, Ruixin Xu, Liangpeng Nie, Baoping Zhang, Yi Wang,*421 *Shuang Wang, Gang Wang, Jinxiang Diao, Lirong Zheng, Jinbo Bai, Kunyue Leng*, Xiaolin*422 *Li* and Yunteng Qu**

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425 **Materials and Methods**426 **1. Materials:**

427 All chemicals were analytical grade and without further purification. Analytical grade Sodium

428 tungstate dihydrate, Ruthenium(III) chloride trihydrate, dopamine hydrochloride, Hydrogen

429 chloride and potassium hydroxide were obtained from Innochem. Commercial Pt/C (20 wt%),

430 Ru/C (5 wt%) and Nafion were acquired from Sigma-Aldrich.

431 **2. Synthesis of Ru-W/WO₂-800:**

432 Firstly, 2 mmol of dopamine hydrochloride was dissolved in 20 ml of deionized water, and

433 the pH value was adjusted to 2 by adding 800 μl HCl (1 mol L⁻¹). Then, 0.1 mmol of RuCl₃·434 xH₂O was added to the solution and mixed by stirring to obtain a homogeneous solution.435 After that, 20 ml Na₂WO₄·2H₂O solution (0.1 mol L⁻¹) was slowly dropped into the solution

436 under vigorous stirring. A large amount of brown precipitate formed immediately. The

437 reaction was further stirred for 1 h, the obtained product was collected by centrifugation,

438 washed with deionized water and ethanol 3 times. The precursor was dried in an oven at 60 °C

439 overnight and heated at 800 °C for 2 h in Ar atmosphere at a heating rate of 2 °C/min.

440 **3. Synthesis of WO₂-800:**441 WO₂ was prepared without the addition of any other metal salts followed by the same442 synthetic approach of Ru-W/WO₂-800.443 **4. Synthesis of Ru₁/WO₂-800:**444 Firstly, 100 mg WO₂-800 were mixed with 50 mL ethanol and stirred for 0.5 h. After that, 2445 mg RuCl₃· xH₂O was added in solution and further stirred for 12 h. Then, evaporated the

446 solvent to dryness at 70 °C, and kept the obtained sample under Ar atmosphere at 350 °C for 2
447 h.

448 **5. Synthesis of Ru SACs catalysts:**

449 In a typical synthesis, 3 ml NH₄OH, 80ml ethanol and 180ml deionized water were mixed by
450 stirring 10 minutes. Following, 10ml pure dopamine solution (40 mg ml⁻¹) and 10 ml Ru
451 contained dopamine solution (DA=40 mg ml⁻¹, Ru=0.43 mg ml⁻¹) were slowly alternate
452 dropped into the solution under vigorous stirring. The reaction was further stirred for 12 h and
453 gradually formed brown precipitation under stirring. The obtained product was collected by
454 centrifugation, washed with deionized water and ethanol 3 times. The precursor was dried in
455 an oven at 60 °C overnight and heated at 800 °C for 5 h in Ar atmosphere at a heating rate of
456 2 °C/min.

457 **6.Characterization:**

458 Scanning electron microscopy (SEM) images were obtained on a FEI Apreo S microscope.
459 Transmission electron microscopy (TEM) and high-resolution transmission electron
460 microscope (HR-TEM) images were collected with a Talos F200X microscope. Aberration-
461 corrected scanning transmission electron microscopy (AC HAADF-STEM) images were
462 collected with a JEOL JEM-ARM200F microscope. The X-ray diffraction (XRD, Bruker D8
463 Advance) was used to analyze crystal structures. X-ray photoelectron spectroscopy (XPS)
464 measurements were conducted on a PHI 5000 Versa spectrometer using Al K α radiation. The
465 metal contents in the catalysts were determined by Inductively Coupled Plasma Optical
466 Emission Spectrometer (ICP-OES) on a Agilent 5110.X-ray absorption fine structure (XAFS)
467 measurements for the Ru K-edge, W L3-edge were performed on beamline 1W1B of Beijing
468 Synchrotron Radiation Facility. The acquired EXAFS data were extracted and processed
469 according to the standard procedures using the ATHENA module implemented in the
470 IFEFFIT software packages. Operando Raman spectra were measured under controlled
471 electrochemical potentials using a three-electrode epoxy cell with a counter electrode of Pt
472 wire and Ag/AgCl. A controlled active area of 0.384 cm² by an insulation layer on carbon
473 paper drop-casted with 0.1 mg catalyst was used as the working electrode. Raman spectra
474 were collected using a Raman spectrometer (WITEC Alpha500) by a 633 nm He-Ne laser
475 (Research Electro-Optics, Inc., USA) at the objective. A 20 \times microscope objective lens
476 (NA=0.4, Epiplan-Neofluar, Zeiss, Germany) was used, focusing on the sample surface and
477 avoiding the contact to the electrolyte. Acquisition time was set as 20 s for the spectral Raman
478 shift ranging from 800 to 1,800 cm⁻¹ window a UHTS300 spectrometer (WITec GmbH,

479 Germany) with a CCD camera (Andor Technology, UK) operating at -60 °C. The downward
480 shift ratio and the theoretical value was calculated based on the equation below:

$$\gamma = \frac{\nu(\text{RuD})}{\nu(\text{RuH})} = \frac{\sqrt{m(\text{Ru}) + m(\text{D})}}{\sqrt{m(\text{Ru}) \times m(\text{D})}} \div \frac{\sqrt{m(\text{Ru}) + m(\text{H})}}{\sqrt{m(\text{Ru}) \times m(\text{H})}}$$

481 Where γ represents the downward shift ratio, ν represents the Raman shift, m represents the
482 relative molecular mass.

483 7. Electrochemical measurement:

484 All the electrochemical measurements were carried out in a conventional three-electrode cell
485 using the CHI 760E electrochemical workstation at room temperature. A rotating disk
486 electrode (RDE) with a glassy carbon (GC) electrode (diameter: 5 mm; area: 0.196 cm²) was
487 utilized as the working electrode (WE), and the Pt plate was used as the counter electrode.
488 The Ag/AgCl reference electrode calibrated with RHE in 1 M KOH was used as a reference
489 electrode for long-time stability measurement. For electrode preparation, 10 mg of Ru-
490 W/WO₂-800 catalyst was dispersed in the mixture solution of IPA (400 μ l) and 5 wt.% Nafion
491 (20 μ l) by sonication for over 30 minutes. Then, 10 μ l of the catalyst ink was drop-cast onto
492 the surface of the GC electrode and dried in the air. Linear sweep voltammetry (LSV) plots
493 were carried out in an Ar saturated 1.0 M KOH with a sweep rate of 1 mV s⁻¹ at 1600 rpm.
494 All of the potentials in LSV are 100% iR-corrected. The resistance for iR-compensation was
495 tested at the open circuit potential, Ru-W/WO₂-800 (9.3 Ω), Ru₁@WO₂-800 (8.3 Ω), Pt/C
496 (8.0 Ω), Ru/C (8.4 Ω), Ru SACs (8.9 Ω) and WO₂-800 (8.3 Ω). All the potentials were
497 converted to the reversible hydrogen electrode (RHE) by equation.

$$498 \quad V_{\text{RHE}} = E_{(\text{VS Ag/AgCl})} + 0.197 + 0.0592 \cdot \text{pH}$$

499 The Tafel slope was obtained the LSV curve using the equation of $\eta = a + b \log j$, where a refers
500 to the intercept, b is the Tafel slope and η denotes the overpotential. Electrochemical
501 impedance spectroscopy (EIS) measurements were collected at $\eta = 20$ mV in the frequency
502 range from 10 kHz to 0.01 Hz, The Mass activity is calculated based on equation of Mass
503 Activity = I/m , where I (A) is the measured current, m (mg) is the mass of Ru loaded on the GC
504 electrode. The turnover frequency (TOF) is calculated based on the equation of $\text{TOF} = I/(4Fn)$,
505 where I (A) is the measured current. F is the Faraday constant (96485 C mol⁻¹). $n = m/M$, n
506 (mol) is the molar amount of Ru loaded on the GC electrode, m is the mass of Ru, and M is
507 the molecule weight. For the double-layer capacitor (C_{dl}) data, cycling voltammetry (CV)
508 curves were recorded in the non-Faradic region with scanning rate of 5, 10, 15, 20, 25 and 30

509 mV s⁻¹, and the C_{dl} can be obtained by plotting the current difference (Δj) against the scanning
510 rate.

511 **8. Computational Method:**

512 We have employed the first-principles to perform density functional theory (DFT)
513 calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-
514 Ernzerhof (PBE) formulation.^[1-3] We have chosen the projected augmented wave (PAW)
515 potentials to describe the ionic cores and take valence electrons into account using a plane
516 wave basis set with a kinetic energy cutoff of 520 eV.^[4,5] Partial occupancies of the
517 Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05
518 eV. The electronic energy was considered self-consistent when the energy change was smaller
519 than 10⁻⁵ eV. A geometry optimization was considered convergent when the energy change
520 was smaller than 0.05 eV Å⁻¹. In our structure, the U correction is used for W and Ru atoms.
521 The Brillouin zone integration is performed using 2×2×1 Monkhorst-Pack k-point sampling
522 for a structure. Finally, the adsorption energies (E_{ads}) were calculated as E_{ads}= E_{ad/sub} -E_{ad} -E_{sub},
523 where E_{ad/sub}, E_{ad}, and E_{sub} are the total energies of the optimized adsorbate/substrate system,
524 the adsorbate in the structure, and the clean substrate, respectively. The free energy was
525 calculated using the equation:

$$526 \quad G = E_{\text{ads}} + \text{ZPE} - \text{TS}$$

527 where G, E_{ads}, ZPE and TS are the free energy, total energy from DFT calculations, zero-point
528 energy and entropic contributions, respectively. The U correction for W and Ru were used as
529 4.18 and 4.92 eV for d orbital, respectively.

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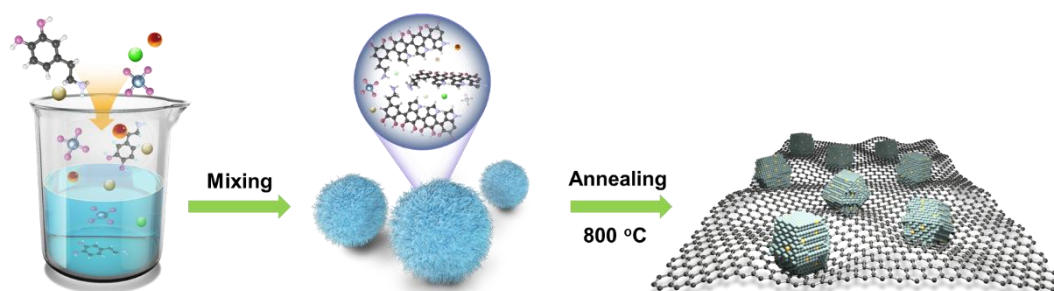
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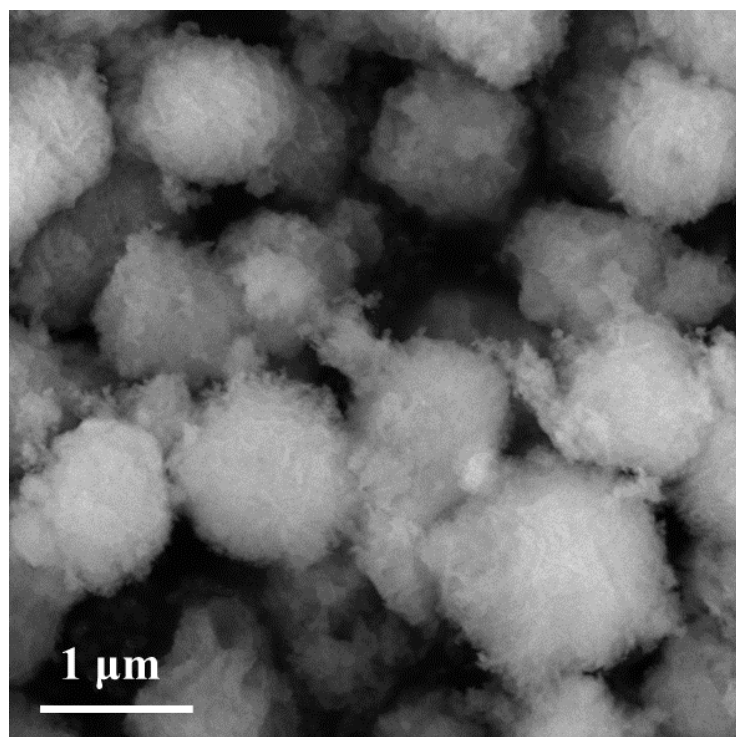
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Supplementary Figures



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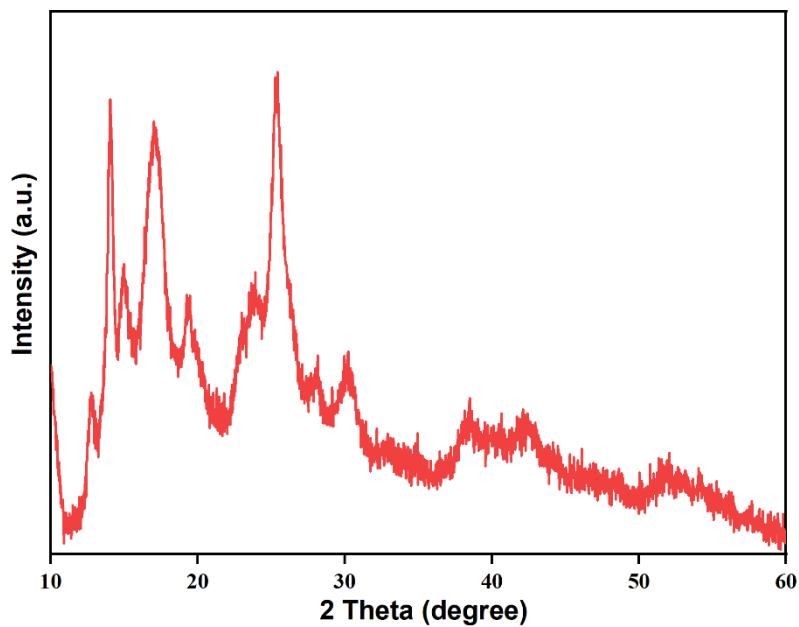
Figure S1. Illustration of the synthetic process of dual-atom Ru-W catalyst.



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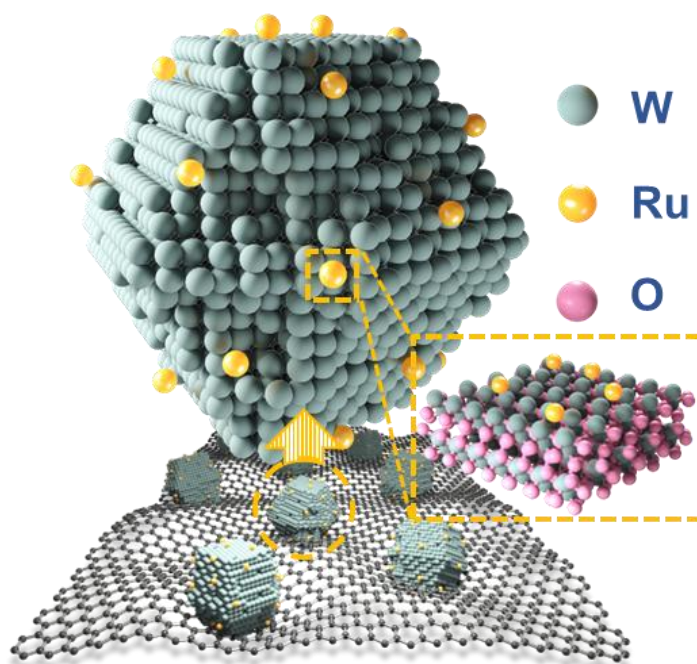
Figure S2. SEM image of as obtained mixture of polydopamine, W and Ru.

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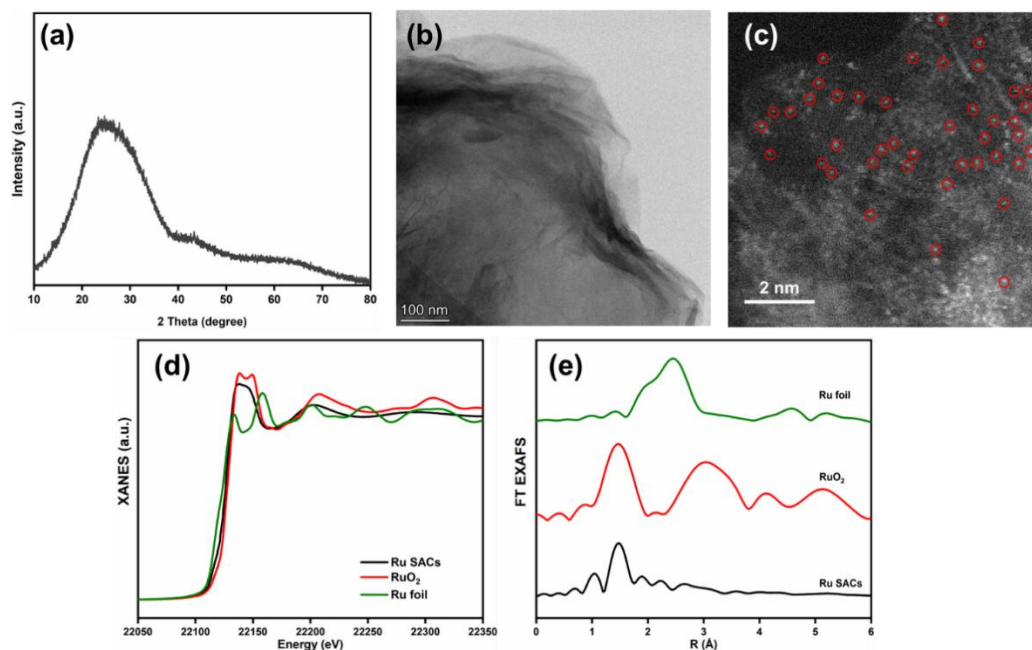
Figure S3. XRD pattern of the as obtained mixture of polydopamine, W and Ru. Only the diffraction peaks belonging to polydopamine were observed.



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583 **Figure S4.** Simulative structure of Ru₁/WO₂-800. Single atom Ru sites randomly disperse on
 584 the surface of WO₂.

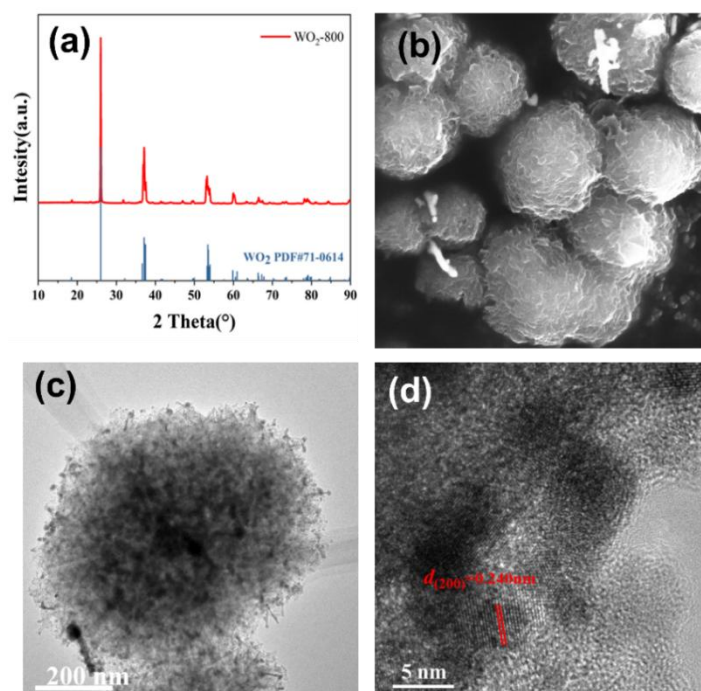
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590 **Figure S5.** Structure identification of Ru SCAs. (a) XRD pattern, (b) TEM image, (c)
 591 Aberration-Corrected HAADF-STEM images, (d) Ru K edge XANES spectrum, (e) Ru K
 592 edge FT EXAFS spectrum.

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Figure S6. Characterization of WO₂-800. (a) XRD pattern, (b) SEM image, (c) TEM image,
 (d) HRTEM image.

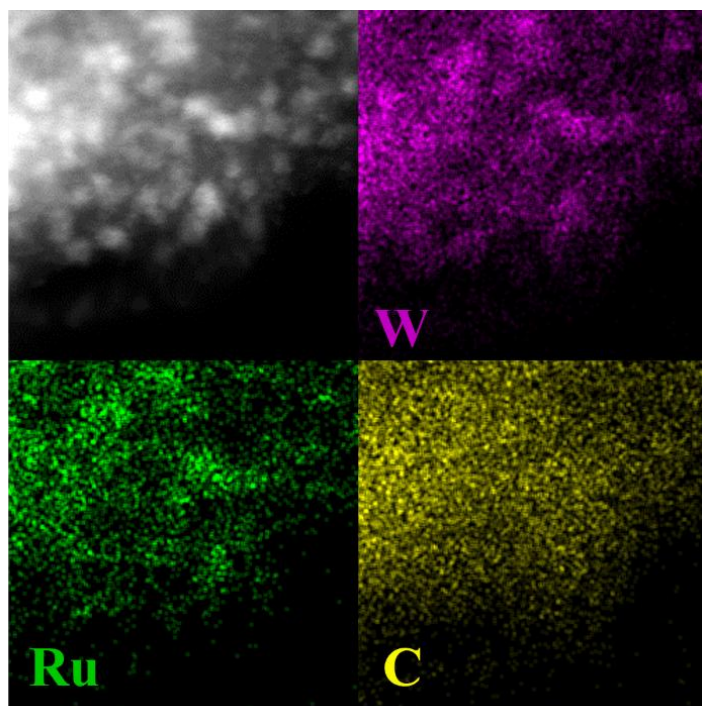


Figure S7. EDS element mapping of Ru-W/WO₂-800.

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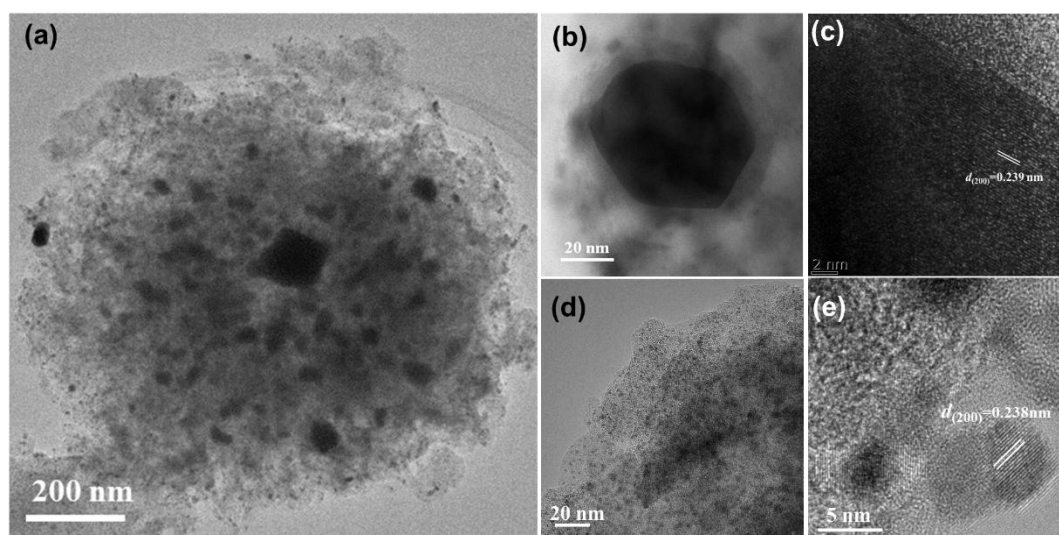
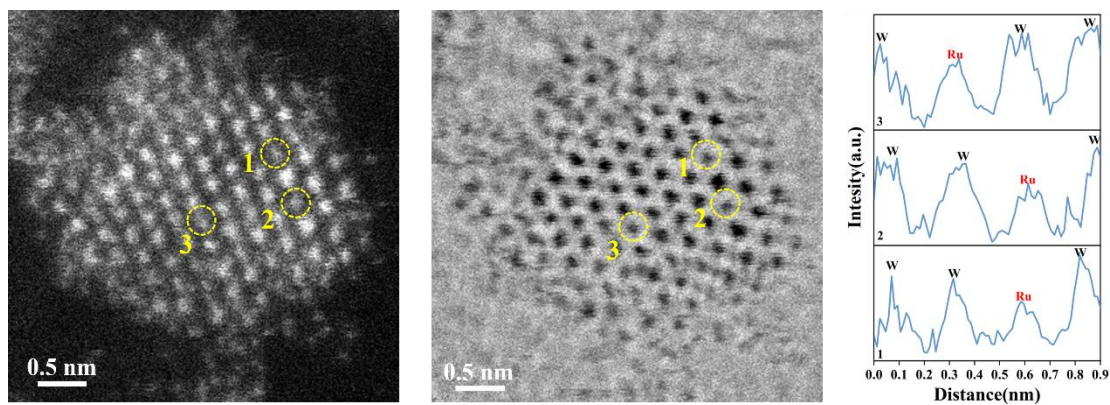


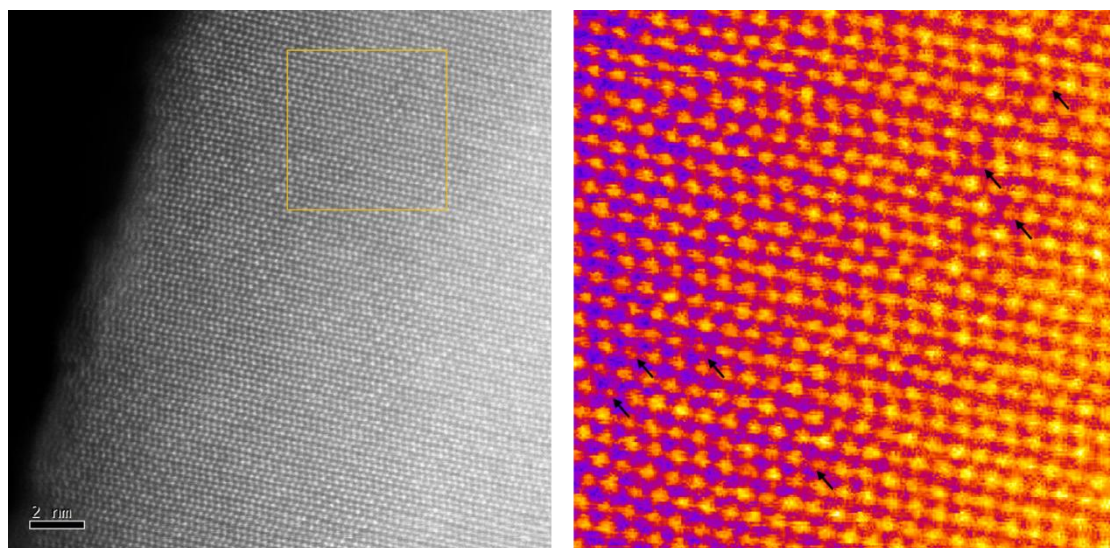
Figure S8. TEM images. (a) Ru-W/WO₂-800. (b, c) WO₂ particle in Ru/WO₂-800. (d, e) WO₂ cluster in Ru/WO₂-800.

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619 **Figure S9.** Dark and bright filed STME images and corresponding line intensity profiles of
620 WO_2 clusters in Ru-W/ WO_2 -800.
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638 **Figure S10.** Aberration-Corrected HAADF-STEM images and corresponding intensity
639 profiles of Ru_1/WO_2 -800
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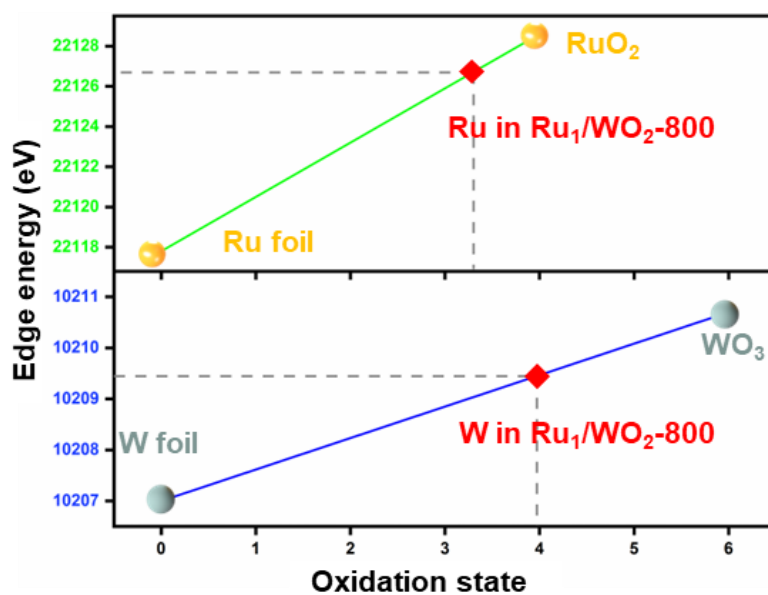


Figure S11. Simulative oxidation state of Ru and W in Ru₁/WO₂-800

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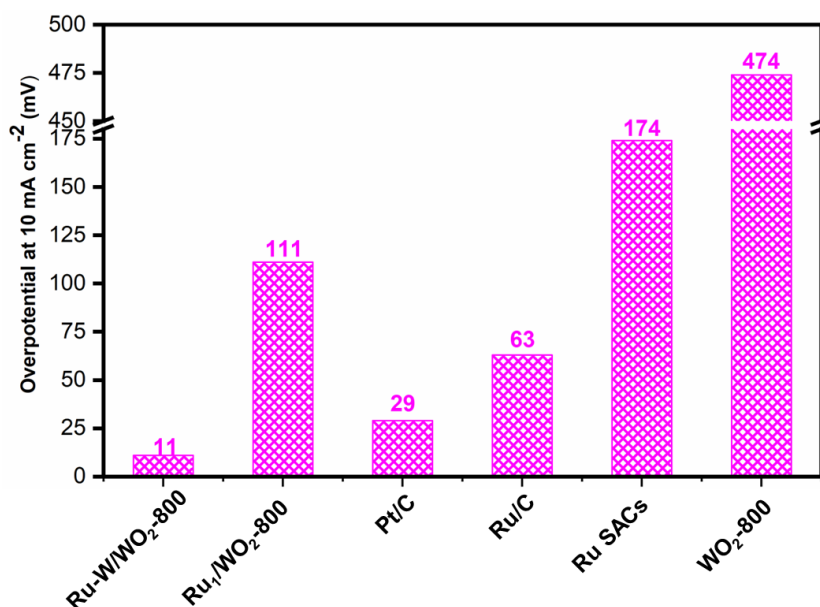
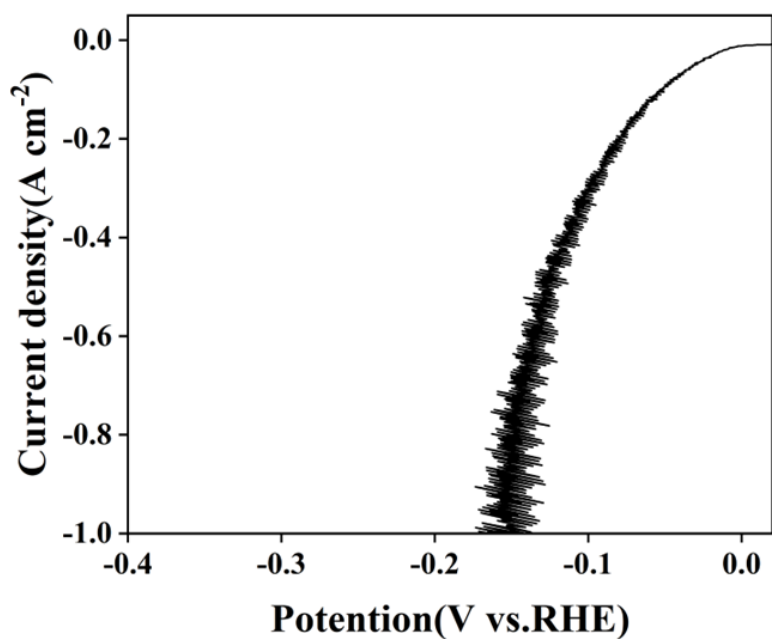
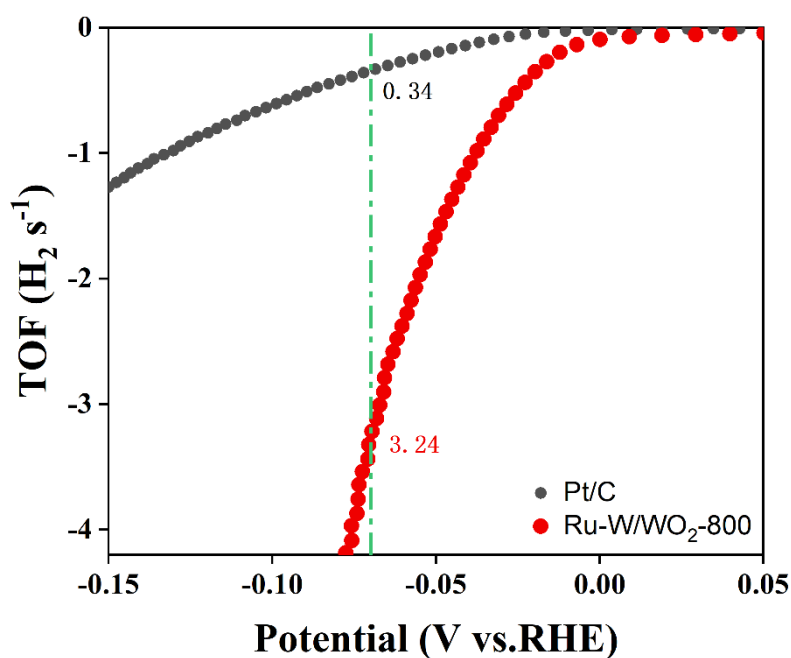


Figure S12. Overpotential of Ru-W/WO₂-800, Ru₁/WO₂-800, Pt/C, Ru/C, Ru SACs and WO₂-800 at a current density of 10 mA cm⁻².

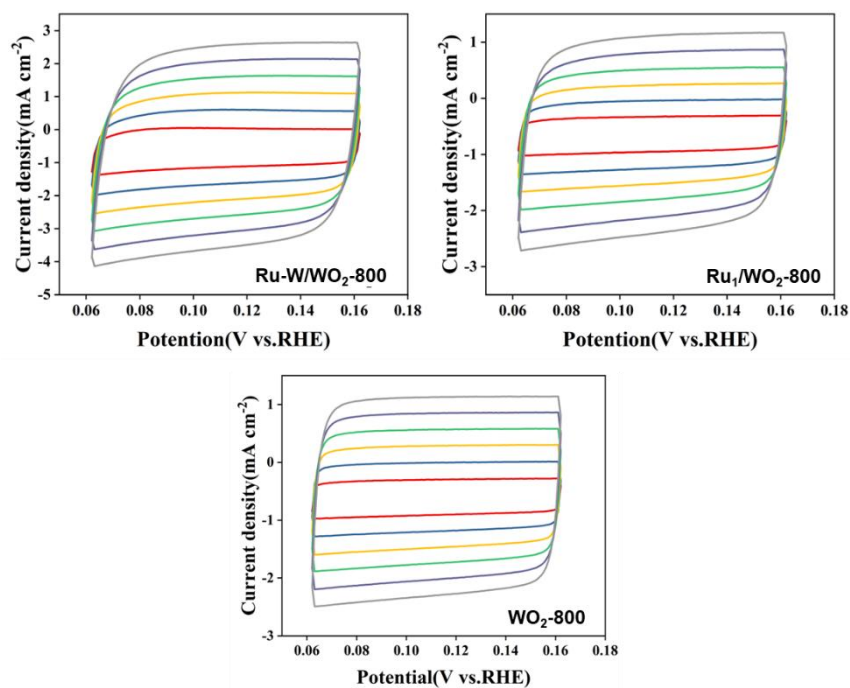
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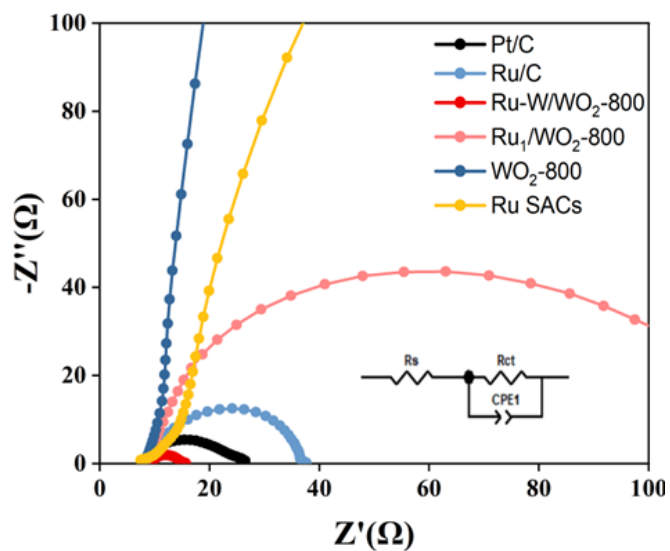
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665 **Figure S13.** LSV curve of Ru-W/WO₂-800 in 1 M KOH under higher current density.
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673 **Figure S14.** The turnover frequency of Ru-W/WO₂-800 and Pt/C for HRE in 1 M KOH.
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683 **Figure S15.** Cyclic voltammetry curves at different scan rates (mV s^{-1}) for Ru-W/ WO_2 -800,
684 Ru_1 / WO_2 -800 and WO_2 -800.
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692 **Figure S16.** Nyquist plots of Ru-W/ WO_2 -800, Ru_1 / WO_2 -800, Pt/C, Ru/C, Ru SACs and
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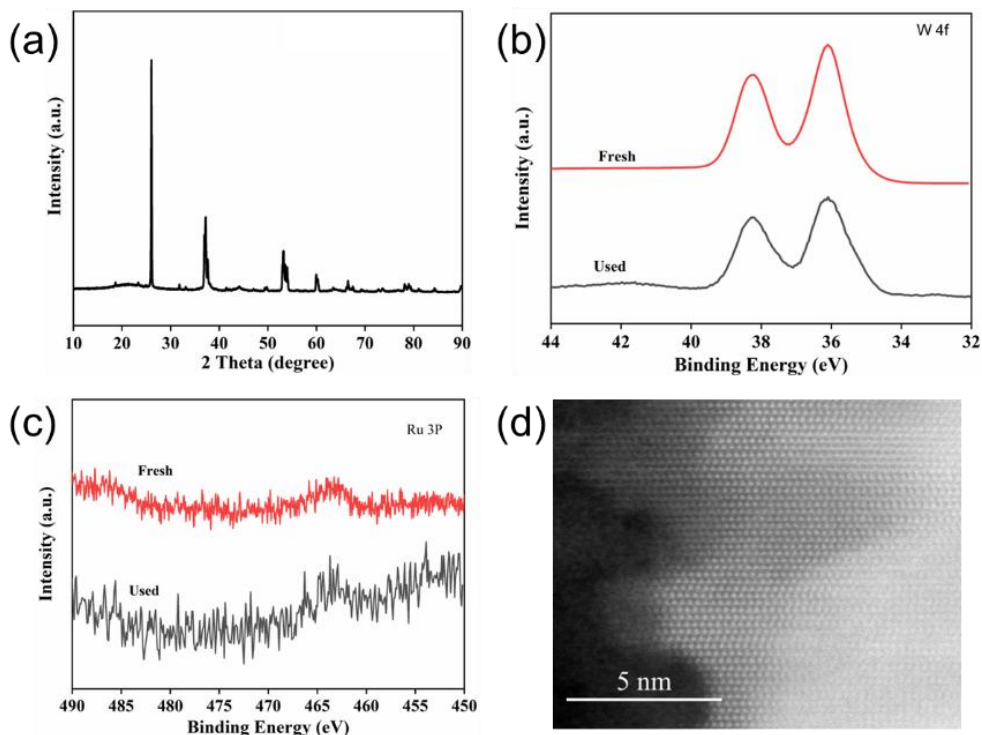


Figure S17. Physical characterization of Ru-W/WO₂ after the long-term test. (a) XRD pattern. (b) W 4f XPS spectra. (c) Ru 3p XPS spectra. (d) HAADF-STEM image.

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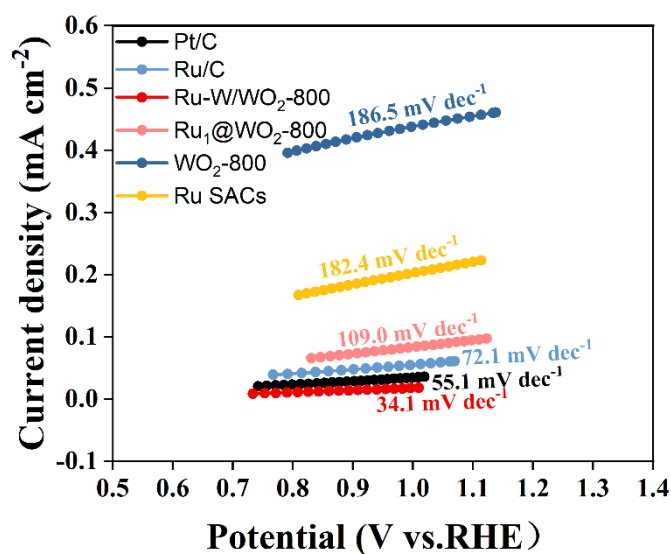
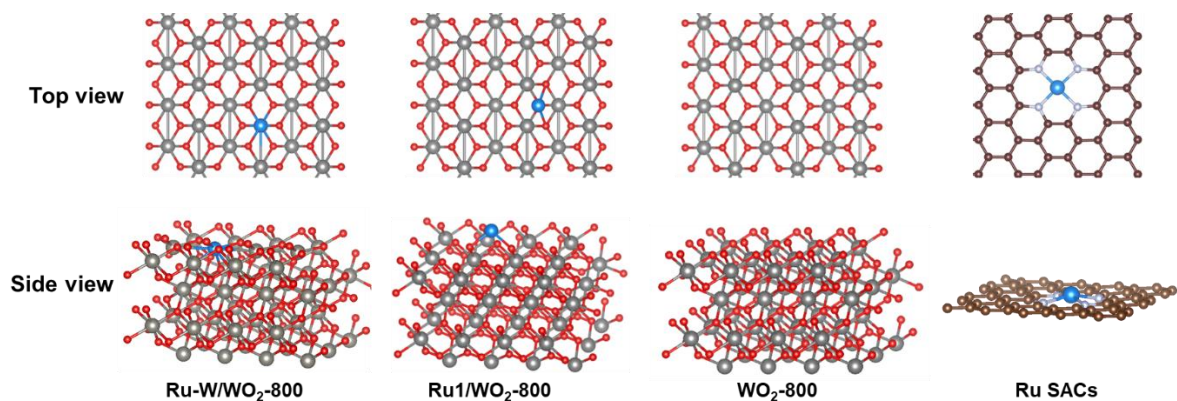


Figure S18. Tafel plots of Ru-W/WO₂-800, Ru₁/WO₂-800, Pt/C, Ru/C, Ru SACs and WO₂-800 in alkaline simulated seawater of 1 M KOH and 0.5 M NaCl.

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Figure S19. Simulative structures of Ru-W/WO₂-800, Ru₁/WO₂-800, WO₂-800, and Ru SACs.

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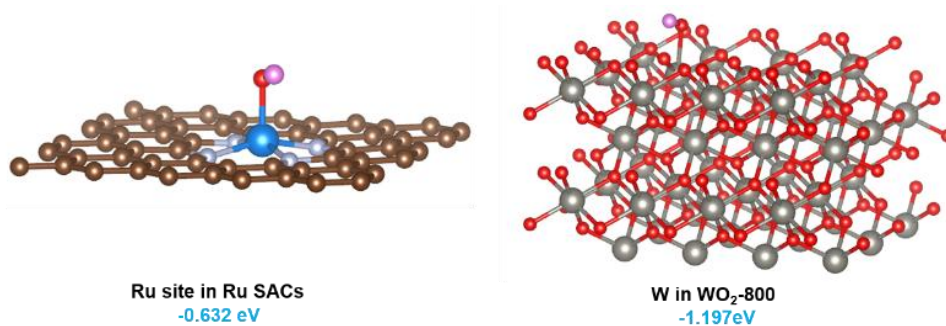
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Figure S20. Simulative structure of OH adsorbed on the Ru SACs and WO₂-800 and the corresponding adsorption energy.

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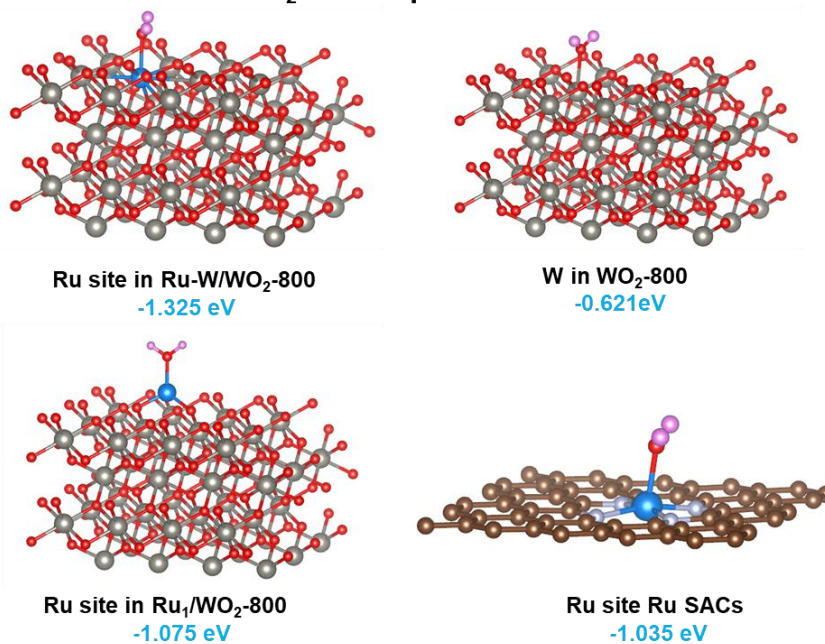
H₂O-adsorption

Figure S21. Simulative structures of H₂O adsorbed on Ru-W/WO₂-800, Ru₁/WO₂-800, WO₂-800 and Ru SACs and the corresponding adsorption energy.

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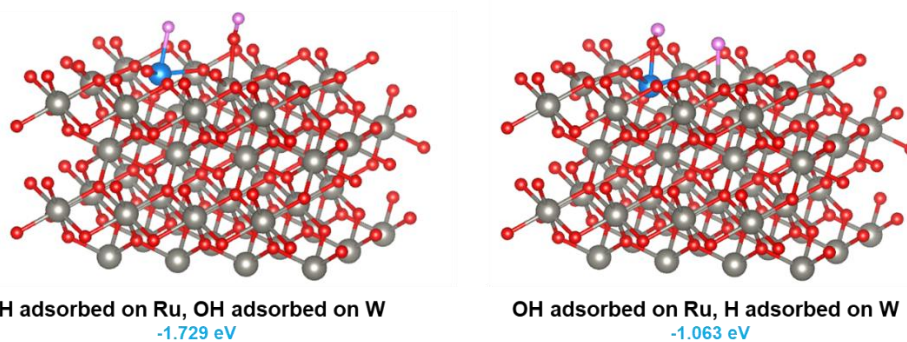


Figure S22. Different adsorption models and the corresponding adsorption energy of water dissociation intermediate (H-OH) on Ru-W/WO₂-800.

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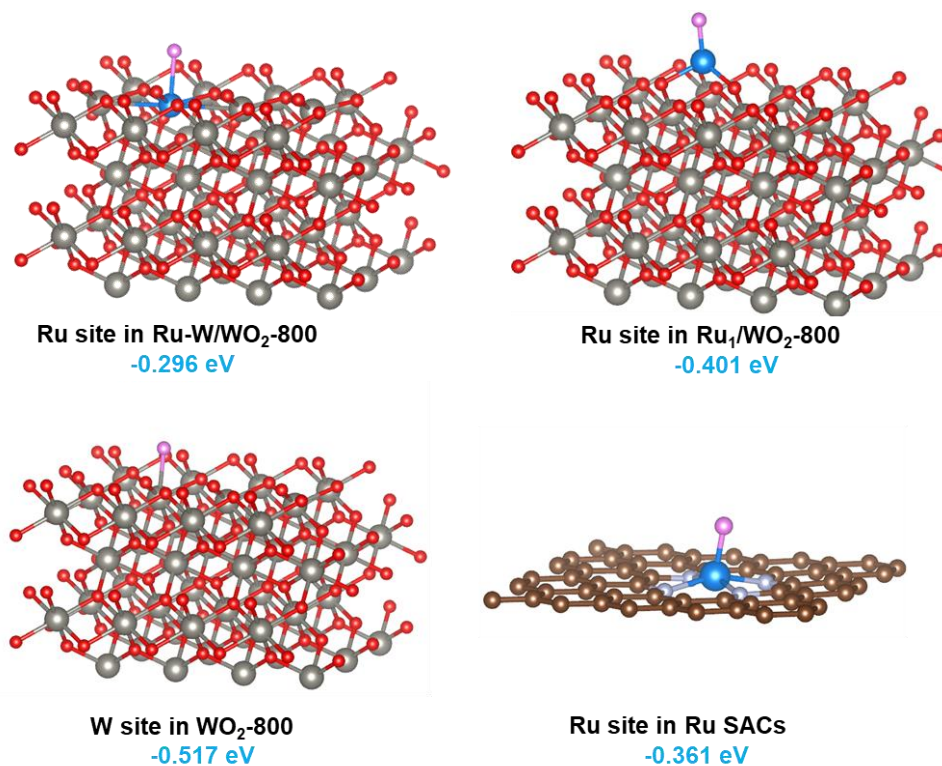
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Figure S23. Simulative H adsorption model and corresponding adsorption energy on Ru and W sites

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Supplementary Tables

Table S1. Metal content in various samples.

Sample	Metal content measured by ICP	
	Ru (wt%)	W (wt%)
Ru-W/WO ₂ -800	1.30	25.00
Ru ₁ /WO ₂ -800	1.27	25.77
Ru SACs	1.37	--

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Table S2. EXAFS fitting parameters at the Ru K-edge for Ru-W/WO₂-800.

Sample	Shell	N ^a	R (Å) ^b	σ^2 (Å ² ·10 ⁻³) ^c	ΔE_0 (eV) ^d
Ru-W/WO ₂ -800	Ru-O	3.1±0.2	2.01±0.03	5.2±3.0	-1.1±0.2
	Ru-W	0.9±0.1	2.79±0.02	1.9±3.0	-2.3±0.2

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^a N: coordination numbers; ^b R: bond distance; ^c σ^2 : Debye-Waller factors; ^d ΔE_0 : the inner potential correction.

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