ELECTROCHEMISTRY

Single-site Pt-doped RuO_2 hollow nanospheres with interstitial C for high-performance acidic overall water splitting

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Realizing stable and efficient overall water splitting is highly desirable for sustainable and efficient hydrogen production yet challenging because of the rapid deactivation of electrocatalysts during the acidic oxygen evolution process. Here, we report that the single-site Pt-doped RuO_2 hollow nanospheres (SS Pt-RuO_2 HNSs) with interstitial C can serve as highly active and stable electrocatalysts for overall water splitting in 0.5 M H_2SO_4. The performance toward overall water splitting have surpassed most of the reported catalysts. Impressively, the SS Pt-RuO_2 HNSs exhibit promising stability in polymer electrolyte membrane electrolyzer at 100 mA cm^{-2} during continuous operation for 100 hours. Detailed experiments reveal that the interstitial C can elongate Ru-O and Pt-O bonds, and the presence of SS Pt can readily vary the electronic properties of RuO_2 and improve the OER activity by reducing the energy barriers and enhancing the dissociation energy of *O species.

INTRODUCTION

Electrocatalytic water splitting, which couples hydrogen evolution reaction (HER) at cathode and oxygen evolution reaction (OER) at anode, has been widely accepted as an important process for the production of hydrogen and the conversion of intermittent energy (*1*–*5*). Generally, the electrocatalytic water splitting can be operated in acidic, alkaline, and neutral conditions, and therefore, the performance is strongly dependent on the electrocatalysts (*6*–*11*). Compared to alkaline water splitting, water splitting in acidic media is critical for polymer electrolyte membrane (PEM) electrolyzer (*12*–*15*), which presents advantages including high gas purity and proton conductivity and small gas crossover, and therefore attracts great attention (*16*, *17*). However, a highly efficient water splitting in acidic media is limited by the disadvantages of sluggish reaction kinetics and harsh acidic and oxidative environments of OER (*18*–*20*). It is thus highly desired to develop robust electrocatalysts for acidic water splitting.

Despite the widespread applications of RuO_2 and IrO_2 for acidic OER (*21*–*23*), RuO_2 has been regarded as a promising catalyst for acidic OER because of its cheaper price and higher activity compared with IrO_2 (*24*, *25*). However, RuO_2 suffers from the drawback of poor stability in acidic media at high potential (*26*). Over the past decades, substantial efforts have been devoted to the modifications of RuO_2 to improve its stability for acidic OER (*27*–*29*). For example, it has been reported that Cu doping into RuO_2 hollow porous polyhedra can substantially improve the OER performance, and the catalyst displays excellent stability within 10,000 cyclic voltammetry (CV) cycles and 8-hour chronopotentiometric test (*30*). Shan *et al.* (*31*) demonstrated that the heterostructured Ru@IrO_x with a strong charge redistribution between strained Ru core and IrO_x shell can serve as a stable catalyst for acidic OER. Despite the fact that great progress has been achieved, the stability of RuO_2 in acidic conditions is still far away from the satisfaction for practical application. Therefore, the development of robust RuO_2-based catalysts for acidic OER is of great importance.

Here, we report that the single-site Pt-doped RuO_2 hollow nanospheres (SS Pt-RuO_2 HNSs) can be applied as high-performance electrocatalysts for overall acidic water splitting, in which the interstitial C is trapped in the gap while Pt replaces partial Ru sites in the form of single site. In particular, when SS Pt-RuO_2 HNSs were used as catalyst for water splitting in 0.5 M H_2SO_4, the required cell voltages are as low as 1.49, 1.59, and 1.65 V for reaching current densities of 10, 50, and 100 mA cm^{-2}, respectively, and their catalytic performance have surpassed most of the reported catalysts for overall water splitting. Detailed characterizations reveal that the presence of interstitial C can elongate Ru-O and Pt-O bonds in SS Pt-RuO_2 HNSs, and the introduced SS Pt strongly affects the electronic properties of RuO_2. Density functional theory (DFT) calculations show that the RuO_2 with SS Pt can significantly enhance the stability and reduce energy barriers for boosting OER activities. This work not only may provide a facile strategy for the modification of RuO_2 by doping SS Pt but also sheds new light on the industrial application of overall water splitting.

RESULTS

Morphological and structural characterizations

The PtRuSe HNSs was initially synthesized via a hydrothermal method, in which hydrazine hydrate aqueous solution and H_2O were used as

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reducing agent and solvent, respectively. The obtained PtRuSe HNSs exhibit a morphology of HNS with a Pt/Ru/Se ratio of 4.7:31.6:63.7, as revealed by transmission electron microscopy (TEM) image and scanning electron microscopy–energy dispersive spectrometer (SEM-EDS) profile (fig. S1). The PtRuSe HNSs were then loaded onto the VC-X72 carbon powder (fig. S2). No obvious x-ray diffraction (XRD) peaks except for some typical bread-shaped diffraction peaks are observed, suggesting the amorphous nature of PtRuSe HNSs (fig. S3). Afterward, the carbon-supported PtRuSe HNSs were treated in air at 300°C for 10 hours to obtain SS Pt-RuO_2 HNSs. No obvious changes in the morphology were observed after this thermal treatment despite the fact that partial carbon was removed, as revealed by the high-angle annular dark-field scanning TEM (HAADF-STEM) (Fig. 1A) and TEM images (Fig. 1B). Results from SEM-EDS spectrum show that the atomic ratio of O/Ru/Pt/Se is 74.9:23.0:1.1:1.0 in SS Pt-RuO_2 HNSs, while the significant decrease of Se in SS Pt-RuO_2 HNSs is ascribed to the evaporation of Se during thermal treatment (fig. S4). The appearance of RuO_2 peaks and the absence of Pt peaks in the XRD pattern of SS Pt-RuO_2 HNSs indicate that Pt atoms are well dispersed on RuO_2 (Fig. 1C). In Raman spectra, the features of E_g, A_{1g}, and B_{2g} of RuO_2 are observed, and the disappearance of D-band and G-band of graphite carbon further confirms that the graphite structure is destroyed and RuO_2 is formed during the heat treatment process (fig. S5) (*32*). Spherical aberration–corrected HAADF-STEM measurement was performed to study the distributions of Pt atoms in SS Pt-RuO_2 HNSs. It is found that Ru atoms are partially replaced by Pt atoms in the form of isolated state (bright dots in Fig. 1D) (*33*, *34*). We further enlarged the selected area in Fig. 1D, and the details of the atomic line profiles further confirm the isolated state of Pt atoms in SS Pt-RuO_2 HNSs (Fig. 1, E to J). The corresponding fast Fourier transform (FFT) pattern of SS Pt-RuO_2 HNSs identifies the exposed (110) and ($\bar{1}01$) planes of RuO_2 along [$\bar{1}1\bar{1}$] zone axis (Fig. 1F), which suggests that Ru and O atoms are arranged with a tetragonal structure (*P42/mnm*) and Pt atoms are exclusively located at Ru position in the manner of single site (Fig. 1G). Moreover, STEM-EDS elemental mapping images suggest that all the elements are evenly distributed in SS Pt-RuO_2 HNSs (Fig. 1K). The absence of carbon shell in the high-resolution TEM (HRTEM) image implies that C has entered into RuO_2 (fig. S6). In addition, PtRuSe HNSs with different Pt atomic ratios were synthesized (denoted as RuO_2 HNSs, 2% Pt-RuO_2 HNSs, and 10% Pt-RuO_2 HNSs, respectively) (figs. S7 to S10). Similarly, the typical peaks of RuO_2 were observed in the XRD patterns and the Raman spectra of all samples. The presence of diffraction peaks of Pt in the XRD pattern of 10% Pt-RuO_2 HNSs suggests that Pt atoms present as nanoparticles

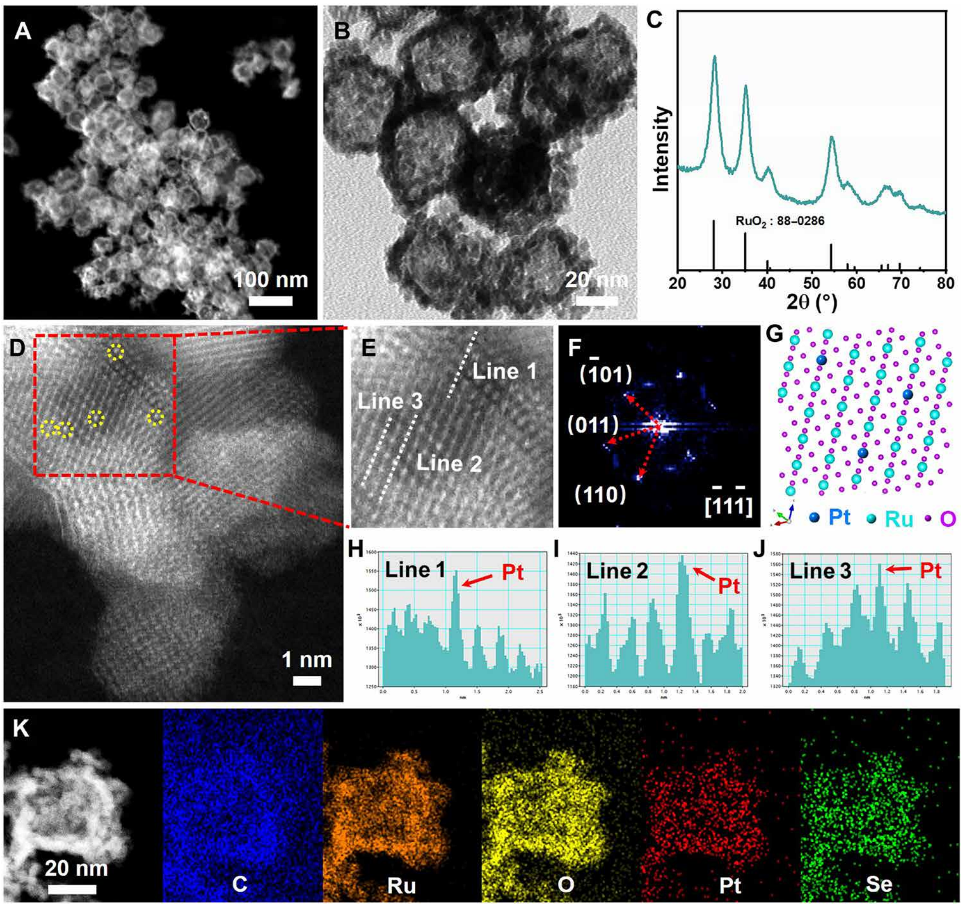

Fig. 1. Morphological and structural characterizations. (**A**) HAADF-STEM image, (**B**) TEM image, (**C**) XRD pattern, and (**D**) high-resolution HAADF-STEM image of SS Pt-RuO_2 HNSs. (**E**) High-resolution HAADF-STEM image obtained from the area highlighted with red rectangles in (D). (**F**) FFT pattern and (**G**) crystal structure model of SS Pt-RuO_2 HNSs. (**H** to **J**) Line-scanning intensity profile obtained from the area highlighted with white lines in (E). (**K**) STEM image and STEM-EDS elemental mapping images of SS Pt-RuO_2 HNSs.

(figs. S11 and S12). The lattice fringes in the HRTEM of 2% Pt-RuO_2 HNSs are ascribed to RuO_2 (101) and (110) planes, respectively (fig. S13). In addition to the lattice distances of RuO_2 (101) and (210) facets, the presences of Pt (111) and Pt (200) lattice distances in the HRTEM image of 10% Pt-RuO_2 HNSs further confirm the existence of Pt nanoparticles (fig. S14).

Catalytic performance

The OER and HER performance of various catalysts were evaluated in 0.5 M H_2SO_4 with standard three-electrode system. As shown in Fig. 2A, SS Pt-RuO_2 HNSs display small overpotentials of 228, 262, and 282 mV for achieving current densities of 10, 50, and 100 mA cm^{-2}, respectively, during OER. In contrast, the overpotentials are 325, 405, and 489 mV at the current densities of 10, 50, and 100 mA cm^{-2} when commercial RuO_2 was used as catalyst (table S1). Moreover, SS Pt-RuO_2 HNSs exhibit the smallest Tafel slope compared to RuO_2 HNSs and commercial RuO_2, suggesting the fastest reaction kinetics of SS Pt-RuO_2 HNSs for OER (Fig. 2B). To evaluate the OER activity, the overpotentials and Tafel slopes of various catalysts were summarized. It is found that SS Pt-RuO_2 HNSs exhibit significantly superior OER performance to RuO_2 HNSs and commercial RuO_2 (Fig. 2C). Moreover, when SS Pt-RuO_2 HNSs was used as catalyst for HER, the overpotentials are 26, 47, and 67 mV at the current densities of 10, 50, and 100 mA cm^{-2}, respectively, which are close to those values of the state-of-the-art Pt/C catalyst (Fig. 2D and table S2). By contrast, the overpotentials of RuO_2 HNSs are 68, 109, and 142 mV for achieving current densities of 10, 50, and 100 mA cm^{-2}, respectively. On the other hand, SS Pt-RuO_2 HNSs display a similar

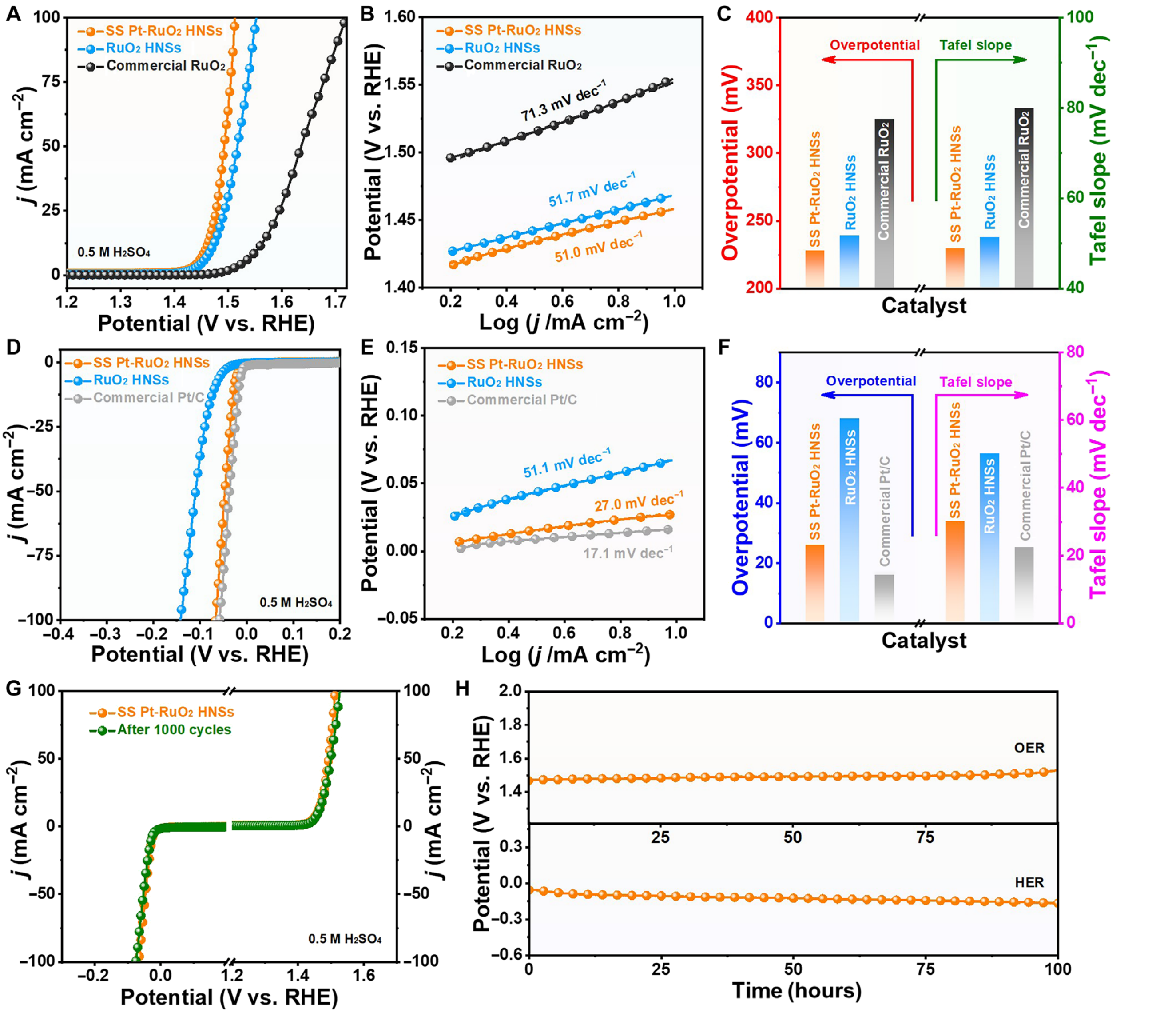

Fig. 2. Electrochemical OER and HER studies. (**A**) OER polarization curves and (**B**) corresponding Tafel slopes of SS Pt-RuO_2 HNS, RuO_2 HNSs, and commercial RuO_2. (**C**) Histogram of overpotentials at 10 mA cm^{-2} and Tafel slopes of various catalysts. (**D**) HER polarization curves and (**E**) corresponding Tafel slopes of SS Pt-RuO_2 HNS, RuO_2 HNSs, and commercial Pt/C. (**F**) Histogram of overpotentials at 10 mA cm^{-2} and Tafel slopes of various catalysts. (**G**) OER and HER polarization curves of SS Pt-RuO_2 HNS before (orange) and after (green) 1000 CV cycles. (**H**) Chronopotentiometry tests of SS Pt-RuO_2 HNS for OER and HER in 0.5 M H_2SO_4 at 10 mA cm^{-2}. RHE, reversible hydrogen electrode

Tafel slope to that of commercial Pt/C, further confirming the excellent HER activity of SS Pt-RuO_2 HNSs (Fig. 2, E and F). Moreover, the electrochemical active surface area of SS Pt-RuO_2 HNSs was evaluated by the double-layer capacitance (C_{dl}) from CV curves in the non-Faradaic region. It is found that the SS Pt-RuO_2 HNSs expose more active sites and therefore exhibit higher activity in comparison to RuO_2 HNSs (fig. S15). Furthermore, Pt-RuO_2 HNSs with different contents of Pt (e.g., 2 and 10%) were used as catalysts for OER and HER. It is noted that both 2% Pt-RuO_2 HNSs and 10% Pt-RuO_2 HNSs exhibit inferior activity and/or stability to SS Pt-RuO_2 HNSs (figs. S16 and S17). In addition, the slight decays in the OER and HER polarization curves after 1000 CV cycles imply the excellent electrocatalytic stability of SS Pt-RuO_2 HNSs (Fig. 2G). Chronopotentiometry tests for HER and OER were carried out at a constant current density of 10 mA cm^{-2} in 0.5 M H_2SO_4 to further investigate the stability of SS Pt-RuO_2 HNSs. For OER, the overpotential of SS Pt-RuO_2 HNSs remains stable for at least 100 hours, while the overpotential of commercial RuO_2 increases sharply after only ~2 hours, indicating the superior stability of SS Pt-RuO_2 HNSs to commercial RuO_2 (Fig. 2H and fig. S18). To demonstrate the significance of the interstitial C on the stability of SS Pt-RuO_2 HNSs, the PtRuSe HNSs were directly treated in air at 300°C for 10 hours without loading on VC-X72 carbon powder. It is noted that the hollow structure of PtRuSe HNSs is completely collapsed (fig. S19A), as a result of poor stability for OER (fig. S19B). The above results suggest the significance of interstitial C on the structural stability. In addition, we further investigated the influence of Se on both the structure and the stability for OER. In the absence of Se precursor (H_2SeO_3), only solid nanoparticles and amorphous carbon were observed after calcination in air at 300°C for 10 hours (fig. S20), indicating that Se plays a crucial role for the formation of SS Pt-RuO_2 HNSs. Besides, we further evaluated the effects of residual Se on the stability for OER through an electrochemical leaching process. As shown in fig. S21A, the atomic ratio of Se significantly decreases to 0.3% after the electrochemical leaching process. No obvious change of potential within 100 hours was observed (fig. S21B) compared to the SS Pt-RuO_2 HNSs without the electrochemical leaching process (Fig. 2H), indicating that the residual Se displays negligible effects on the durability test for OER. With respect to HER, the SS Pt-RuO_2 HNSs exhibits significantly improved stability in 100 hours compared to the commercial Pt/C (fig. S22).

Inspired by the excellent activity and long-term stability, the SS Pt-RuO_2 HNSs were simultaneously used as both cathode and anode catalysts in a two-electrode system for acidic overall water splitting (Fig. 3A). Notably, the SS Pt-RuO_2 HNSs show promising activity for overall water splitting, and the cell voltages are as low as 1.49, 1.59, and 1.65 V for achieving current densities of 10, 50, and 100 mA cm^{-2}, respectively (Fig. 3B). By contrast, the benchmark catalysts of commercial Pt/C for cathode and commercial RuO_2 for anode require a much larger cell voltage of 1.56, 1.67, and 1.77 V for reaching the same current densities. Moreover, the chronopotentiometry tests of SS Pt-RuO_2 HNSs||SS Pt-RuO_2 HNSs and commercial RuO_2||commercial Pt/C were performed in 0.5 M H_2SO_4 to evaluate their stability (Fig. 3C). The required cell voltage for commercial RuO_2||commercial Pt/C at 10 mA cm^{-2} significantly increases after a short period, indicating a sharp decrease of activity. In contrast, SS Pt-RuO_2 HNSs||SS Pt-RuO_2 HNSs shows excellent stability with a small cell voltage increase within 100 hours (table S3). Note that SS Pt-RuO_2 HNSs||SS Pt-RuO_2 HNSs exhibit superior stability to the reported catalysts for overall water splitting in acidic media (Fig. 3D). Furthermore, the morphology and structure of SS Pt-RuO_2 HNSs are largely maintained after water splitting for 100-hour continuous operation (figs. S23 and S24). In sharp contrast, severe Pt agglomeration was observed for commercial Pt/C (note that commercial RuO_2/C generally suffers from poor stability for OER because of Ru dissolution in acidic conditions; fig. S25). In addition, we used SS Pt-RuO_2 HNSs as both cathode and anode catalysts in PEM electrolyzer in pure water to mimic the industrial water splitting operating systems. As shown in Fig. 3E, the chronopotentiometry tests of SS Pt-RuO_2 HNSs||SS Pt-RuO_2 HNSs show high stability without significant cell voltage increase over 100 hours at the current density of 100 mA cm^{-2}, indicating the great potential of SS Pt-RuO_2 HNSs for practical applications (Fig. 3F). In sharp contrast, commercial IrO_2||commercial Pt/C displays obviously inferior stability even in 4 hours at the same conditions (fig. S26).

Mechanism studies

In view of the excellent acidic water splitting activity, the electronic structure of SS Pt-RuO_2 HNSs was investigated by x-ray absorption spectroscopy measurement. The x-ray absorption near-edge structure (XANES) spectra at Pt L_3-edge indicate that Pt species are presented as oxidation state in the SS Pt-RuO_2 HNSs (Fig. 4A). The Fourier transforms of Pt L_3-edge extended x-ray absorption fine structure (EXAFS) spectra reveal that the Pt-O interatomic distance of SS Pt-RuO_2 HNSs is ~1.68 Å, which is larger than that of PtO_2 (Fig. 4B) (*35*). The absence of Pt-Pt coordination in the EXAFS spectrum of SS Pt-RuO_2 HNSs implies that Pt atoms present as isolated state. On the basis of the EXAFS spectra of Se mesh and SeO_2, we can conclude that Se species present as oxidation state in SS Pt-RuO_2 HNSs (Fig. 4C). For Ru, the *K*-edge XANES spectrum of SS Pt-RuO_2 HNSs displays similar features to those of RuO_2, indicating that Ru species in SS Pt-RuO_2 HNSs are in oxidation state. The intensity of the while line for the *K*-edge XANES spectrum of SS Pt-RuO_2 HNSs is slightly higher than that of RuO_2, suggesting the existence of electron transfer between Pt and RuO_2 (Fig. 4D), which is further validated by x-ray photoelectron spectroscopy (XPS) measurement (fig. S27). Compared to RuO_2, the interatomic distance of Ru-O bond in SS Pt-RuO_2 HNSs is expanded, which might be attributed to the formation of C-O bonds with the assistance of interstitial C (Fig. 4E) (*36*). Compared to commercial RuO_2/C, the strengthened intensity for C-O and positive shift of the binding energy in the C 1s XPS spectrum of SS Pt-RuO_2 HNSs suggest a much stronger interaction (fig. S27D). Moreover, the intensity of Ru-O bonds of SS Pt-RuO_2 HNSs is slightly weaker than that of RuO_2, indicating that the coordination environment of Ru is unsaturated, which may be attributed to the formation of oxygen vacancies (O_V) after Se evaporation (*37*–*39*). The formation of O_V in SS Pt-RuO_2 HNSs is further confirmed by O 1s XPS result (fig. S27E). To further study the local structure of O in SS Pt-RuO_2 HNSs, the O *K*-edge XANES spectra were collected. As shown in Fig. 4F, two sharp characteristic peaks at 528.7 and 531.9 eV, which are caused by the influence of crystal field, are assigned to the excitation of O 1s core electrons into hybridized states between O 2p and Ru 4d t_{2g} and e_g states (*40*), while the broad peak at 542.2 eV is attributed to the hybridization of the O 2p orbital with Ru 5sp states (*41*). The wavelet transform analysis further confirms results from EXAFS measurement (Fig. 4, G and H, and fig. S28). On the basis of the above results, the crystal structure of SS Pt-RuO_2 HNSs are provided, in

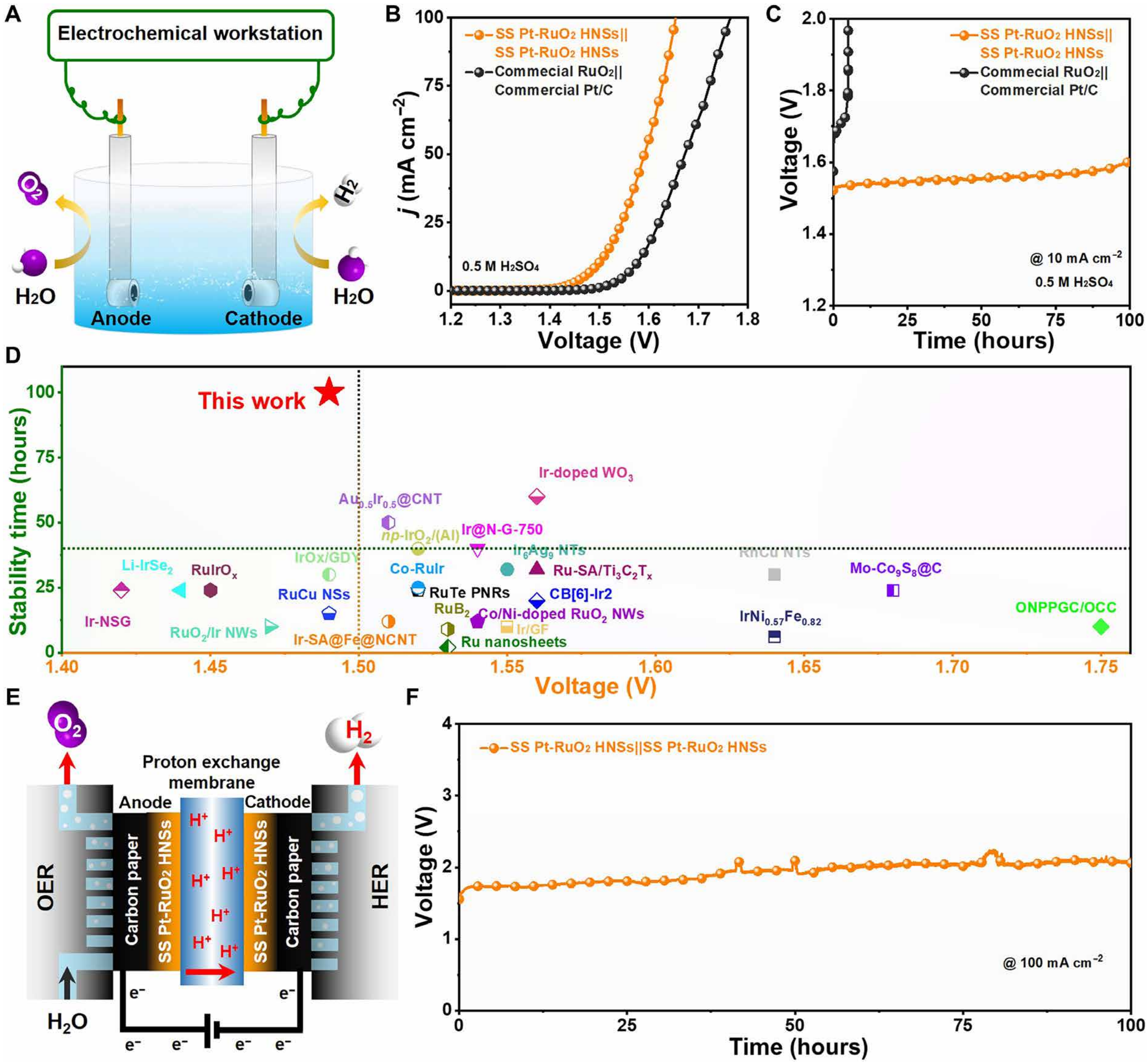

Fig. 3. Catalytic performance of overall water splitting. (**A**) Scheme of the two-electrode cell electrolyzer using SS Pt-RuO_2 HNSs as both the anode and cathode catalyst. (**B**) Polarization curves of SS Pt-RuO_2 HNSs||SS Pt-RuO_2 HNSs and commercial RuO_2||Pt/C in 0.5 M H_2SO_4 for water splitting. (**C**) Chronopotentiometry tests of SS Pt-RuO_2 HNSs||SS Pt-RuO_2 HNSs and commercial RuO_2||Pt/C at 10 mA cm^{-2}. (**D**) Comparison of the voltage and stability between SS Pt-RuO_2 HNSs and other reported catalysts for water splitting in acidic media. (**E**) Schematic diagram of the PEM electrolyzer. (**F**) Chronopotentiometry tests of SS Pt-RuO_2 HNSs||SS Pt-RuO_2 HNSs at 100 mA cm^{-2} in the PEM electrolyzer.

which Ru and O atoms are alternatively arrayed to form octahedral structure with Ru at the center and O at the vertex, while partial Ru atoms are replaced by Pt or Se atoms (Fig. 4I). In addition, C atoms insert into the gap to form interstitial atoms, and the existing interstitial C elongates the Ru-O and Pt-O bonds. Consequently, the strong interactions between SS Pt and RuO_2 significantly vary the electronic properties of catalysts and then improve the catalytic performance.

DFT calculations were performed to deepen the insight of enhanced OER performance on SS Pt-RuO_2 HNSs. Because of strongly oxidative conditions and corrosive electrolytes during operation, the catalyst stability in acidic electrolytes thus plays an important role in electrocatalysis (*42*). Theoretically, the dissociation energy for lattice O directly coordinated to the Ru core is a critical factor for the modeled RuO_2 system in determining the catalyst stability under acidic conditions (*43*). As shown in Fig. 5A, the dissociation energy of *O (i.e., ΔG_O) on SS Pt-RuO_2 HNSs is 1.22 eV higher than that on pure RuO_2, indicating the lattice O atom in SS Pt-RuO_2 HNSs is much more difficult to dissociate in the electrolyte solution. This will be effectively beneficial to enhance the stability of RuO_2 during electrocatalysis. Moreover, the superior reaction activity for SS Pt-RuO_2 HNSs to that of pure RuO_2 can be understood by using the energy change of potential determining step (PDS), that is, the formation of *OOH during OER reaction (*44*). As shown in Fig. 5B, the calculated ΔG for PDS on RuO_2 and SS Pt-RuO_2 HNSs are 2.02 and 1.738 eV, respectively, indicating that the doping of isolated Pt atoms can reduce energy barriers for OER, being consistent with the experimental observations. To deeply understand the origin of the enhanced OER activity for Pt-RuO_2, the Bader charge analysis

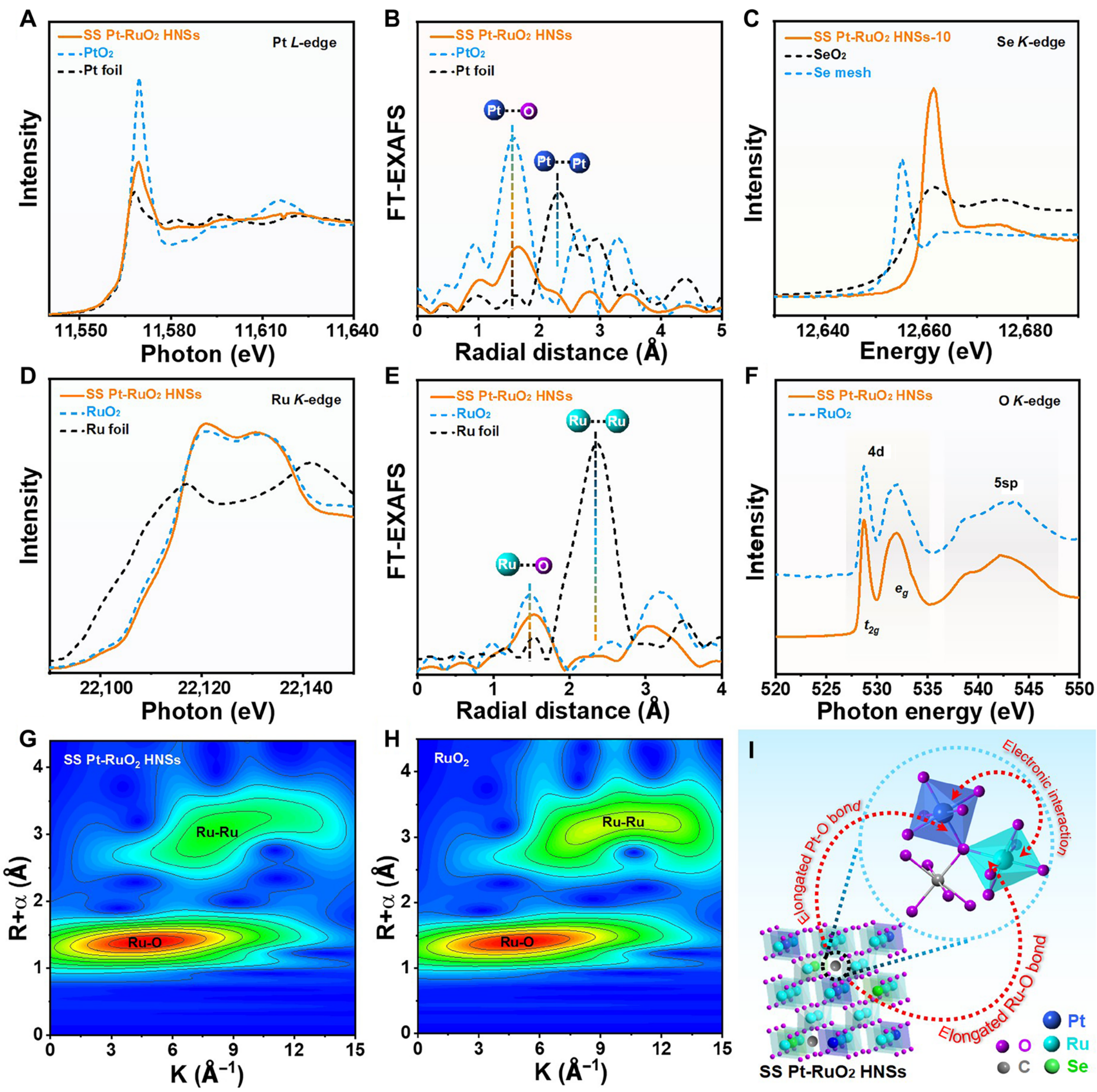

Fig. 4. Structural analysis of the catalysts. (**A**) Pt L_3-edge XANES and (**B**) Pt L_3-edge EXAFS spectra of SS Pt-RuO_2 HNSs, PtO_2, and Pt foil. (**C**) Se *K*-edge XANES spectra of SS Pt-RuO_2 HNSs, SeO_2, and Se mesh. (**D**) Ru *K*-edge XANES and (**E**) Ru *K*-edge EXAFS spectra of SS Pt-RuO_2 HNSs, commercial RuO_2, and Ru foil. (**F**) O *K*-edge XANES spectra of SS Pt-RuO_2 HNSs and commercial RuO_2. Wavelet transform of Ru *K*-edge EXAFS data of (**G**) SS Pt-RuO_2 HNSs and (**H**) commercial RuO_2. (**I**) Structural illustration of SS Pt-RuO_2 HNSs.

for pure RuO_2 and RuO_2 decorated with Pt single atom (Pt-RuO_2) were performed. We defined the SD (σ) of the charge numbers of O atoms as the descriptor to quantify the asymmetry degree. We found that the σ value in Pt-RuO_2 increases to 0.20 after loading Pt single atom, which is much larger than that of pure RuO_2 (0.16), indicating that the charge redistribution and charge density difference are attributed to the introduction of Pt single atom (Fig. 5C and fig. S29A). Moreover, the different electronic distribution will further affect the density of states (DOS). Hence, the Projected density of states (PDOS) for surface-active Ru atoms in pure RuO_2 and Pt-RuO_2 were calculated. As shown in Fig. 5D and fig. S29B, the 4d orbitals of active Ru atoms in Pt-RuO_2 are much closer to Fermi level than pure RuO_2, leading to the improved OER activity. On the basis of experimental and computational analysis, a possible acidic OER mechanism is proposed in Fig. 5E. At the beginning, water molecules will be readily adsorbed on the surface of SS Pt-RuO_2 HNSs. Hydrogen will be removed, and the electrons will be simultaneously generated to form M-O* species. With the participation of water molecules, M-O* will further evolve into M-OOH* and then to form O_2 after electron generation and dehydrogenation.

DISCUSSION

In summary, an ultrastable acidic water splitting electrocatalyst has been successfully created by doping SS Pt into RuO_2. The SS Pt-RuO_2 HNSs not only exhibit excellent OER and HER activity and stability but also show promising acidic water splitting performance in 0.5 M H_2SO_4. The required cell voltages of SS Pt-RuO_2 HNSs are 1.49, 1.59, and 1.65 V for reaching current densities of 10, 50, and 100 mA cm^{-2}, respectively, and their catalytic performance have

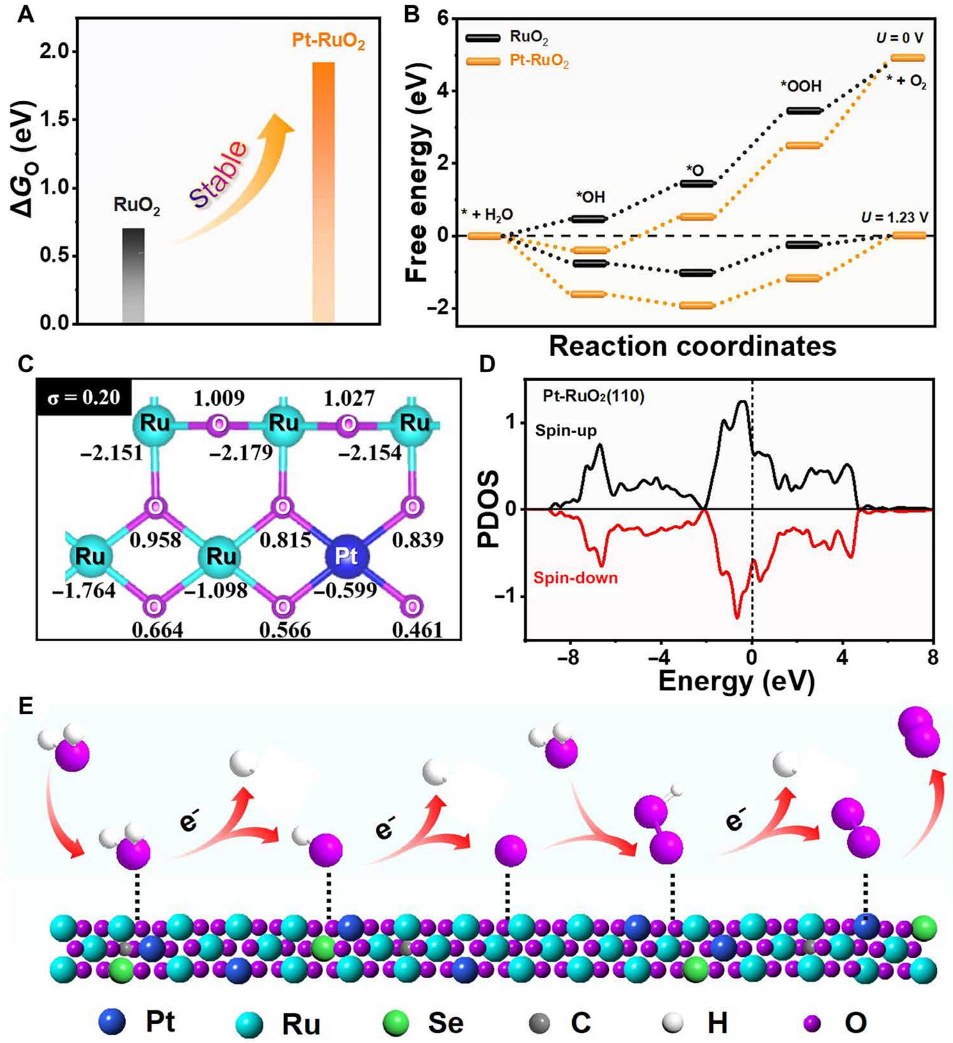

Fig. 5. DFT calculations. (**A**) The calculated dissociation energy of *O in RuO_2 and Pt-RuO_2, respectively. (**B**) The free energy profiles of OER process on RuO_2 and SS Pt-RuO_2 HNSs under the applied overpotential of 0 and 1.23 V (RHE), respectively. (**C**) The Bader charge numbers of atoms in Pt-RuO_2. Note that the negative value is referred to lose electrons, while the positive value mains to obtain electrons. (**D**) The PDOS of 4d orbitals of surface Ru atoms in Pt-RuO_2. (**E**) Schematic illustration of the mechanism for acidic OER on SS Pt-RuO_2 HNSs.

surpassed most reported catalysts. The SS Pt-RuO_2 HNSs exhibit excellent stability in 100 hours of continuous operation at 10 mA cm^{-2} and 100 hours in PEM electrolyzer at the current density of 100 mA cm^{-2}. Detailed experiments reveal that the presence of interstitial C can elongate the Ru-O and Pt-O bonds, and the introduced SS Pt significantly influences the electronic interaction of RuO_2. Theoretical calculations indicate that the strong synergy readily improves the OER activity by reducing the energy barriers and enhancing the dissociation energy of *O species. This work not only may provide a facile strategy for the modification of RuO_2 by doping SS Pt but also sheds new light on the practical application of overall water splitting.

MATERIALS AND METHODS

Chemicals

Hexaammineruthenium (III) chloride ($Cl_3H_{18}N_6Ru$, Ru 32.1%) was purchased from Alfa Aesar. Tetraammineplatinum (II) nitrate ($H_{12}N_6O_6Pt$, Pt 50%) was purchased from Beijing Hwrk Chemical Co. Ltd. Selenious acid (H_2SeO_3, 98%) was purchased from Sigma-Aldrich. Hydrazine hydrate aqueous solution ($N_2H_4{\cdot}H_2O$, AR) and isopropanol (IPA; AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. Poly(vinylpyrrolidone) (PVP; average molecular weight 58,000, K15-19) was purchased from J&K Scientific Ltd.

Preparation of PtRuSe HNSs

For the preparation of PtRuSe HNSs, 7.7 mg of $Cl_3H_{18}N_6Ru$, 6.5 mg of H_2SeO_3, 0.5 mg of $H_{12}N_6O_6Pt$, and 50.0 mg of PVP were added into a mixture solution containing 10.0 ml of H_2O and 0.12 ml of N_2H_4 with ultrasonic treatment for 20 min. Then, the mixture solution was transferred into Teflon-sealed autoclave and heated at 180°C for 12 hours. Subsequently, the mixed solution was centrifuged and washed with ethanol/acetone.

Preparation of SS Pt-RuO_2 HNSs

The PtRuSe HNSs were added into a suspension consisting of carbon powders (VC-X72) and ethanol, and then, the above suspension was sonicated for 30 min. Subsequently, the carbon-supported PtRuSe HNSs were centrifuged and dried at 60°C in a vacuum oven. Last, the carbon-supported PtRuSe HNSs were placed in a tube furnace and annealed at 300°C in air for 10 hours to obtain SS Pt-RuO_2 HNSs. Other PtRuSe HNSs synthesized by controlling the amount of $H_{12}N_6O_6Pt$ were selected for the preparation of pure RuO_2 HNSs, 2% Pt-RuO_2 HNSs, and 10% Pt-RuO_2 HNSs, respectively.

Characterizations

A Hitachi HT7700 TEM with an accelerating voltage of 120 kV was used to conduct low-magnification TEM analysis. The atomic structures of the SS Pt-RuO_2 HNSs images were taken on JEM-ARM200F with a cold-field emission gun and a spherical aberration corrector. HAADF-STEMs were conducted on a FEI Tecnai F20 TEM with an acceleration voltage of 200 kV. XRD analysis was carried out on X'Pert-Pro MPD diffractometer (PANalytical, Netherlands) with Cu Kα radiation. Raman spectra were carried out on a Raman spectrometer (LabRam HR 800) using 633-nm laser.

Electrochemical measurements

All the electrochemical tests were carried out on CHI660 workstation (CHI Instruments Inc., Shanghai) in 0.5 M H_2SO_4. HER and OER measurements were conducted with a standard three-electrode system. The overall water splitting measurements were carried out with a two-electrode setup. The ink was prepared by dispersing the catalyst to be tested homogeneously into the solution including 195 μl of IPA and 5 μl of Nafion (5%), followed by sonication for 30 min. The work electrode was prepared by dropping the ink (loading amount about 60 μg_{Ru}) onto the surface of the glassy carbon electrode (diameter, 5 mm). Graphite rod and saturated calomel electrode are used as counter and reference electrode, respectively. All polarization curves are the average of the stable polarization curves scanned in three experiments with 95% iR compensation.

DFT calculations

The quantum mechanics calculations were carried out using the VASP software at the version of 5.4.4, with the Perdew, Burke, and Ernzerhof flavor of DFT (*45*). The projector augmented wave method was used to account for core-valence interactions (*46*–*48*). The kinetic energy cutoff for plane wave expansions was set to 400 eV, and reciprocal space was sampled by the gamma-centered *k*-mesh with a grid of 3 × 3 × 1. The vacuum layer is at least 15 Å in the *z* direction to minimize possible interactions between the replicated cells. The convergence criteria are 1×10^{-5} eV energy differences for solving the electronic wave function. The Methfessel-Paxton smearing of second order with a width of 0.1 eV was applied. All geometries (atomic coordinates) were converged to within 1×10^{-2} eV Å^{-1} for maximal components of forces. A post-stage Van der Waals DFT-D3 method with Becke-Johnson damping was applied (*49*).

Our simulation model was taken from the experimental RuO_2 structure with lattice parameters of $a = b = 4.54$ Å, $c = 3.13$ Å, respectively. For pure RuO_2, A 3 × 3 × 4 RuO_2 (110) surface slab model was constructed, with the bottom two layers fixed and the top two layers relaxed. Note that the (110) surface has two kinds of Ru site; one site is saturated with six oxygen atoms, and another site was cooperated with five oxygen atoms, which is the active site. For SS Pt-RuO_2 HNSs, one surface Ru atom near the active site was replaced by Pt to mimic the experimental observed structure.

Adsorption behavior of *O, *OH, and *OOH intermediates for each catalyst and each model was optimized to convergence. The ΔG for each OER step was calculated through the model of computational hydrogen electrode along with the equation as follows

$$\Delta G = \Delta E_{\mathrm{DFT}} + \Delta \mathrm{ZPE} - T\Delta S$$

where ΔE_{DFT}, ΔZPE, ΔS, and T are the changes in DFT total energy, zero-point energy, entropy from the initial state to the final state, and temperature, respectively. ΔZPE and ΔS can be obtained by the NIST-JANAF thermodynamics table for gaseous molecules and by calculating the vibrational frequencies for the reactive intermediates, respectively (*50*). The entropy of the chemisorbed intermediates only takes the vibrational entropy into account. The formula for calculating the dissociation energy of *O (ΔG_{O}) is given as follows

$$\Delta G_{\mathrm{O}} = G_{\mathrm{sur}} + (G_{\mathrm{H2O}} - G_{\mathrm{H2}}) - G(^*{}_{\mathrm{O}})$$

where G_{sur}, $G(^*{}_{\mathrm{O}})$ G_{H2O}, and G_{H2} represent the surface energy without absorbate, the energy that adsorbs the structure of *O intermediate, the energy for water molecules, and the energy for hydrogen molecules, respectively.

SUPPLEMENTARY MATERIALS

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