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## Self-driven dual hydrogen production system based on a bifunctional single-atomic Rh catalyst†

Xianyun Peng,<sup>ab</sup> Yuying Mi,<sup>b</sup> Xijun Liu,<sup>id \*c</sup> Jiaqiang Sun,<sup>id d</sup> Yuan Qiu,<sup>b</sup> Shusheng Zhang,<sup>id e</sup> Xiaoxing Ke,<sup>id f</sup> Xinzhong Wang<sup>\*a</sup> and Jun Luo<sup>id \*b</sup>

Electrocatalytic hydrogen evolution is an efficient and economical technology to address environmental contamination and energy crises, but the development of such a high-efficiency and energy-saving sustainable hydrogen production system remains a great challenge. Here, we present a novel strategy to design a self-driven dual hydrogen production system for efficient hydrogen production based on highly-dispersed single Rh atoms supported on an oxygen-functionalized  $\text{Ti}_3\text{C}_2\text{O}_x$  MXene (Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$ ) catalyst. The bifunctional Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$  catalyst exhibits remarkable catalytic activities towards both the pH-universal hydrogen evolution reaction (HER) and hydrazine oxidation reaction (HzOR). Using Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$  as the electrode in the self-driven dual hydrogen production system by combining a Zn– $\text{H}_2$  battery and overall hydrazine splitting units, an ultra-high  $\text{H}_2$  generation rate of 45.77 mmol  $\text{h}^{-1}$  can be achieved. Density functional theory calculations indicate that the atomically dispersed single Rh atoms not only make the free energy of adsorbed H ( $\Delta G_{\text{H}}$ ) more thermoneutral for the HER but also largely decrease the free-energy barrier of the dehydrogenation of adsorbed  $\text{NHNH}_2$  for the HzOR.

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### Introduction

Rapidly increasing energy consumption and the concerns over the deteriorating global environmental situation have driven the demand for clean and sustainable energy sources. Hydrogen ( $\text{H}_2$ ), an energy carrier with a high energy density and zero carbon emissions, has attracted growing attention as a vital fascinating candidate for preventing global warming and environmental crisis.<sup>1–4</sup> The development of  $\text{H}_2$  production approaches has become a research hotspot in recent years. Among the strategies that have been developed to date, electrocatalytic overall water/hydrazine splitting (OWS/OHZS), involving the hydrogen evolution reaction (HER) and water/

hydrazine evolution reaction (OER/HzOR), is deemed as a suitable and green process, and has thus received much attention.<sup>5–8</sup>

Despite the electrocatalytic OWS and OHZS for hydrogen production having been well developed to date, they are commonly driven by outsourcing electricity directly, which conflicts with sustainable development goals. Numerous efforts have been devoted to generating  $\text{H}_2$  by fabricating clean and efficient self-driven  $\text{H}_2$  production systems using integrated energy storage devices, such as solar energy, rechargeable Zn–air batteries, and direct hydrazine fuel cells.<sup>9–13</sup> However, these strategies are all limited to a single compartment with a cathode for catalyzing the HER with a relatively low  $\text{H}_2$  production rate. Besides this, it should be noted that the  $\text{H}_2$  production rate in the OWS unit is largely restricted by the sluggish kinetics of the anodic OER involving a four-electron-transfer process, compared with those of the OHZS process.<sup>2,14–16</sup> A further improvement in the production rate by constructing an advanced self-driven system is more preferential for commercial applications, but also extremely challenging.

Inspired by these pioneering advancements, herein we demonstrate for the first time a self-driven dual hydrogen production system by the introduction of a Zn– $\text{H}_2$  battery. The Zn– $\text{H}_2$  battery can not only produce  $\text{H}_2$ , but can also generate electricity. Thermodynamically, the reduction potential of the  $\text{H}^+/\text{H}_2$  redox couple on the cathode and the one of the  $\text{Zn}^{2+}/\text{Zn}$  couple on the anode are 0 and  $-1.25$  V versus the standard hydrogen electrode (vs. SHE), respectively. For the Zn– $\text{H}_2$  battery, the theoretical cathode potential ( $E_c$ ) and theoretical

<sup>a</sup>Information Technology Research Institute, Shenzhen Institute of Information Technology, Shenzhen 518172, China. E-mail: wangxz@szit.com.cn

<sup>b</sup>Institute for New Energy Materials & Low-Carbon Technologies and Tianjin Key Lab for Photoelectric Materials & Devices, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China. E-mail: jl原因@email.tjut.edu.cn

<sup>c</sup>MOE Key Laboratory of New Processing Technology for Non-Ferrous Metals and Materials and Guangxi Key Laboratory of Processing for Non-Ferrous Metals and Featured Materials, School of Physical Science and Technology, Guangxi University, Nanning 530004, China. E-mail: xjliu@tjut.edu.cn

<sup>d</sup>State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

<sup>e</sup>College of Chemistry, Zhengzhou University, Zhengzhou 450000, China

<sup>f</sup>Beijing Key Laboratory of Microstructure and Properties of Solids, Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing 100124, China

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anode potential ( $E_a$ ) can be calculated as 0.035 V and  $-1.285$  V, respectively. Thus, the theoretical electromotive force ( $E_{\text{emf}} = E_c - E_a$ ) of the battery can be confirmed as 1.32 V. However, it is hard for the voltage to drive the OWS due to the sluggish kinetics and high theoretical thermodynamic potential of the anodic OER of 1.23 V *versus* the reversible hydrogen electrode (*vs.* RHE).<sup>17–20</sup> Fortunately, replacing the OER with the HzOR and forming an OHZS system can sharply decrease the operating voltage due to its unique feature of the ultra-low theoretical oxidation potential of  $-0.33$  V *vs.* RHE.<sup>21–24</sup> Therefore, a self-driven dual hydrogen production system can be constructed by combining a Zn–H<sub>2</sub> battery and OHZS, which can generate hydrogen efficiently on two cathodes (the Zn–H<sub>2</sub> battery and OHZS electrolytic cell) simultaneously with high energy efficiency.

To realize such a concept system, the cathode must be highly active toward both the HER and OHZS. However, the state-of-art platinum (Pt) catalyst is expensive and exhibits low metal atom utilization. Recently, single-atom catalysts (SAs) have been shown to exhibit extraordinary HER activity benefitting from maximum metal atom utilization, low coordination, and good reactivity. Therefore, downsizing nanocatalysts to atomically dispersed atoms is an effective strategy to achieve a comparable HER performance to that of the commercial Pt/C catalyst and greatly reduce the costs of catalysts containing noble metals by reducing the loading of noble metals. Here, a single atom Rh immobilized Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> MXene (Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>) catalyst was applied considering that Rh-based nanomaterials not only have excellent Pt-like catalytic performance for the HER,<sup>25,26</sup> but also excellent HzOR catalytic activity.<sup>27</sup> Electrochemical measurements confirmed that Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> exhibits superior electrocatalytic activities toward both the pH-universal HER and HzOR. Benefiting from the good electrochemical performances of the designed catalyst, an asymmetric alkali–acid Zn–H<sub>2</sub> battery was constructed, which exhibits a high peak power density of 110.8 mW cm<sup>-2</sup> at 175 mA cm<sup>-2</sup> and a large specific capacity of 802.4 mA h g<sub>Zn</sub><sup>-1</sup> at a current density of 10 mA cm<sup>-2</sup>. More importantly, a proof-of-concept self-driven dual hydrogen production system was constructed by the combined utilization of a Zn–H<sub>2</sub> battery to drive OHZS for H<sub>2</sub> production. Unexpectedly, an ultra-high H<sub>2</sub> generation rate of 45.77 mmol h<sup>-1</sup> can be achieved under ambient conditions using the assembled self-driven dual hydrogen production system. The theoretical calculations further provide detail on the fundamental origins of the excellent HER and HzOR performances of the single-atomic Rh catalysts.

## Results and discussion

### Synthesis and characterization of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst

The schematic for synthesizing the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst is illustrated in Fig. 1a. In the first step, the Rh precursor (RhCl<sub>3</sub>·xH<sub>2</sub>O) was added during the exfoliating process of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets from a MAX phase Ti<sub>3</sub>AlC<sub>2</sub> using LiF/HCl.<sup>28,29</sup> Then, the resulting composite was treated with KOH, which can effectively induce the production of a rapid flocculate of the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets due to the great change in pH value.

More importantly, the introduced base replaces the residual –F groups with concentrated –OH in aqueous solution.<sup>30,31</sup> Finally, the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst was obtained *via* annealing treatment of the alkalized composites under an Ar atmosphere. The Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst was also obtained *via* the same procedure as that of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, except that the Rh precursor was not added (please see the Methods section for more details).

The X-ray diffraction (XRD) patterns in Fig. S1† show that the dominant peaks of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> are the same as those of the Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, in which the strong peak of the (002) plane below 10° accompanied by peaks for the (004) and (110) planes indicate the successful synthesis of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>.<sup>32–35</sup> As shown in Fig. 1b, the typical two-dimensional (2D) nanosheet morphology was confirmed from the transmission electron microscopy (TEM) image of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>. The clear and well-defined outline with highly transparent features indicates the ultrathin nature of the material. No obvious Rh nanoparticle formation was observed in the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> nanosheets. Furthermore, the lateral sizes of these 2D nanosheets are hundreds of nanometers, while the thickness of these 2D nanosheets is approximately 2 nm, as determined from the atomic force microscopy (AFM) images (Fig. 1c and S2†), consistent with the TEM analysis results and demonstrating the successful synthesis of the ultrathin Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> nanosheets.

To verify that the Rh species in the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst are atomically dispersed in the nanosheets, aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) characterization was performed. The high-resolution HAADF-STEM images show that ultrasmall bright spots are uniformly distributed on the nanosheets (Fig. 1d), suggesting the presence of isolated single Rh atoms in the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst. Scanning transmission electron microscopy-energy dispersive X-ray (STEM-EDX) mapping shows the existence and uniform distribution of Ti, C, O, and Rh elements in the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst (Fig. S3†). The Rh loading was determined to be 0.17 wt% by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. N<sub>2</sub> adsorption–desorption isotherms were recorded to investigate the surface area and porosity of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (Fig. S4†). As shown, the as-prepared Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst shows typical hybrid-type IV isotherms with a high N<sub>2</sub> uptake at both low and high pressures. The Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> exhibits the highest Brunauer–Emmett–Teller (BET) surface area of 441.81 m<sup>2</sup> g<sup>-1</sup>, with a pore volume of 0.333 cm<sup>3</sup> g<sup>-1</sup>. This feature contributes towards the exposure of active sites and benefits rapid electrochemical reaction. Besides this, Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (specific surface area: 416.61 m<sup>2</sup> g<sup>-1</sup>; pore volume: 0.397 cm<sup>3</sup> g<sup>-1</sup>; prominent pore size: 2.5 nm) exhibits a similar pore structure and specific surface area properties to those of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, which provides higher comparability for the electrochemical performance comparison of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> and Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>.

To verify and explore the electronic structure and coordination environment of the isolated dispersed Rh SAs in the Rh SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst at the atomic level, we performed X-ray absorption fine structure (XAFS) measurements at the Rh K-edge. As shown in the X-ray absorption near-edge structure (XANES) spectra (Fig. 1e), the absorption edge position of the

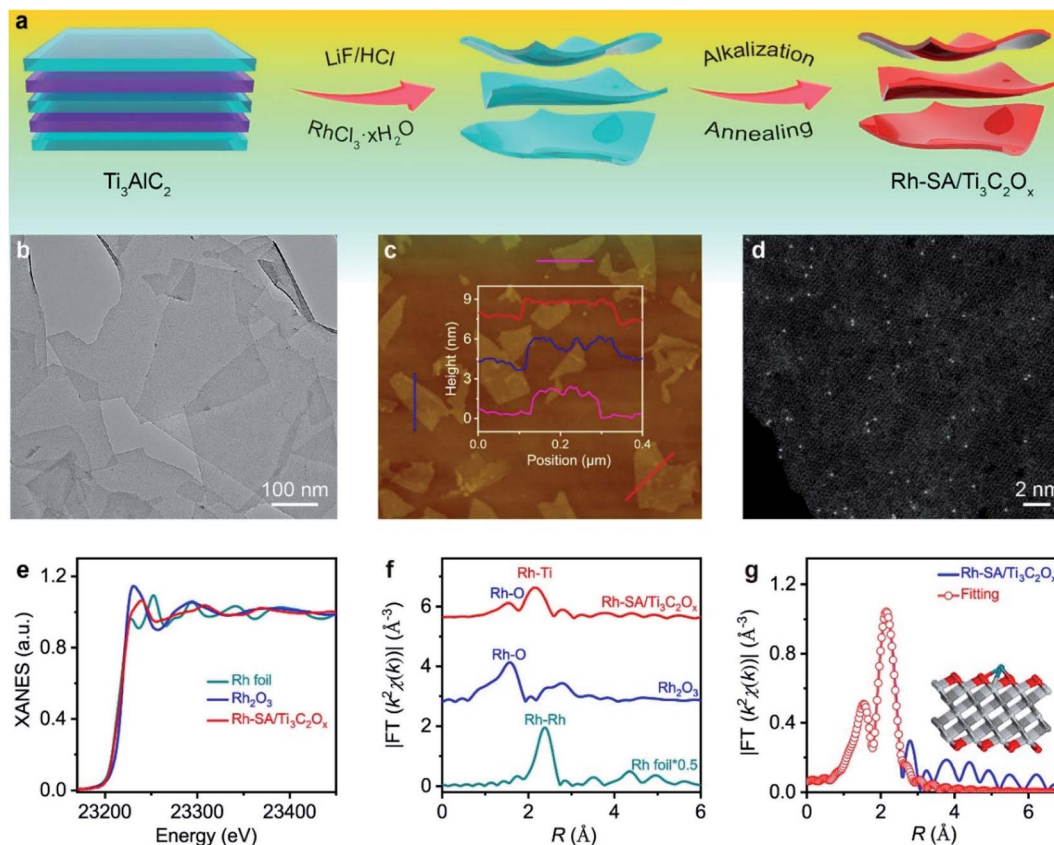


Fig. 1 Synthesis and structural characterization of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst: (a) scheme of the synthesis of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>; (b) AFM image, the inset shows the corresponding height profiles; (c) TEM image of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>; (d) aberration-corrected HAADF-STEM image; (e) Ru K-edge XANES spectra of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst and Rh foil, as well as Rh<sub>2</sub>O<sub>3</sub> references; (f) FT-EXAFS  $k^2$ -weighted  $\chi(k)$  function spectra of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> and those of reference samples; (g) the corresponding FT-EXAFS fitting curves of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>.

white line for Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> is located between those of the Rh foil and Rh<sub>2</sub>O<sub>3</sub> (Fig. S5<sup>†</sup>), indicating that the valence state of the Rh SAs is situated between that of Rh<sup>0</sup> and Rh<sup>3+</sup>. Fig. 1f shows the Rh Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectra of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> and the reference samples. The spectrum of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> exhibits two main peaks at around 1.5 and 2.2 Å, associated with the first shell of Rh–O scattering and the higher shell of Rh–Ti, respectively. Compared to the FT-EXAFS spectrum of Rh foil, no reflection from the Rh–Rh contribution is observed, which further demonstrates that the Rh species in the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst are atomically dispersed without aggregation.<sup>36,37</sup> Furthermore, the coordination environment of the atomically-dispersed centers was further quantified by least-squares EXAFS curve-fitting analysis (Fig. 1g and Table S1<sup>†</sup>). As shown, the best-fitted results of the  $R$ -space spectrum for Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> depict the proposed coordination structure of Ti–Rh–O<sub>3</sub> with Rh–O and Rh–Ti bonds (Fig. 1g, inset).

### Evaluation of the HER performance

The electrocatalytic performance of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst towards the HER was examined using a typical three-electrode system in an acidic medium using Ag/AgCl as the reference

electrode (the electrode was carefully calibrated to the RHE) and graphite rod as the counter electrode. The commercial Pt/C with a Pt loading of 20 wt%, Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (Fig. S6<sup>†</sup>), and Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (Fig. S7<sup>†</sup>) were also been investigated as references. Fig. 2a shows the  $iR$ -compensated linear sweep voltammetry (LSV) curves recorded at a scan rate of 10 mV s<sup>-1</sup> in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution. As displayed, the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst exhibits extraordinary catalytic activity towards the HER, with a near-zero onset potential. To rationally compare the catalytic performance, the HER catalytic activity was normalized to the “current/metal loading mass” (A mg<sup>-1</sup>). Notably, the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst exhibits much higher HER catalytic activity than Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> and even surpasses the performance of the commercial Pt/C catalyst (Fig. 2b) and the majority of the reported HER electrocatalysts (Table S2<sup>†</sup>). In detail, Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> exhibits an overpotential ( $\eta$ ) of 23 mV at a current density of  $-10$  mA cm<sup>-2</sup> (Fig. 2c), 65 mV lower than that of Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (88 mV) and 50 mV lower than that of commercial Pt/C (73 mV), indicating the superior catalytic activity of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> in acidic media. Also, Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> exhibits excellent HER performance at high current densities, as shown in Fig. 2c. Moreover, the mass activities for Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, and commercial Pt/C at an overpotential of 0.1 V are  $-141.58$ ,  $-0.57$ , and  $-2.72$  A mg<sup>-1</sup>, respectively, where Rh-SA/

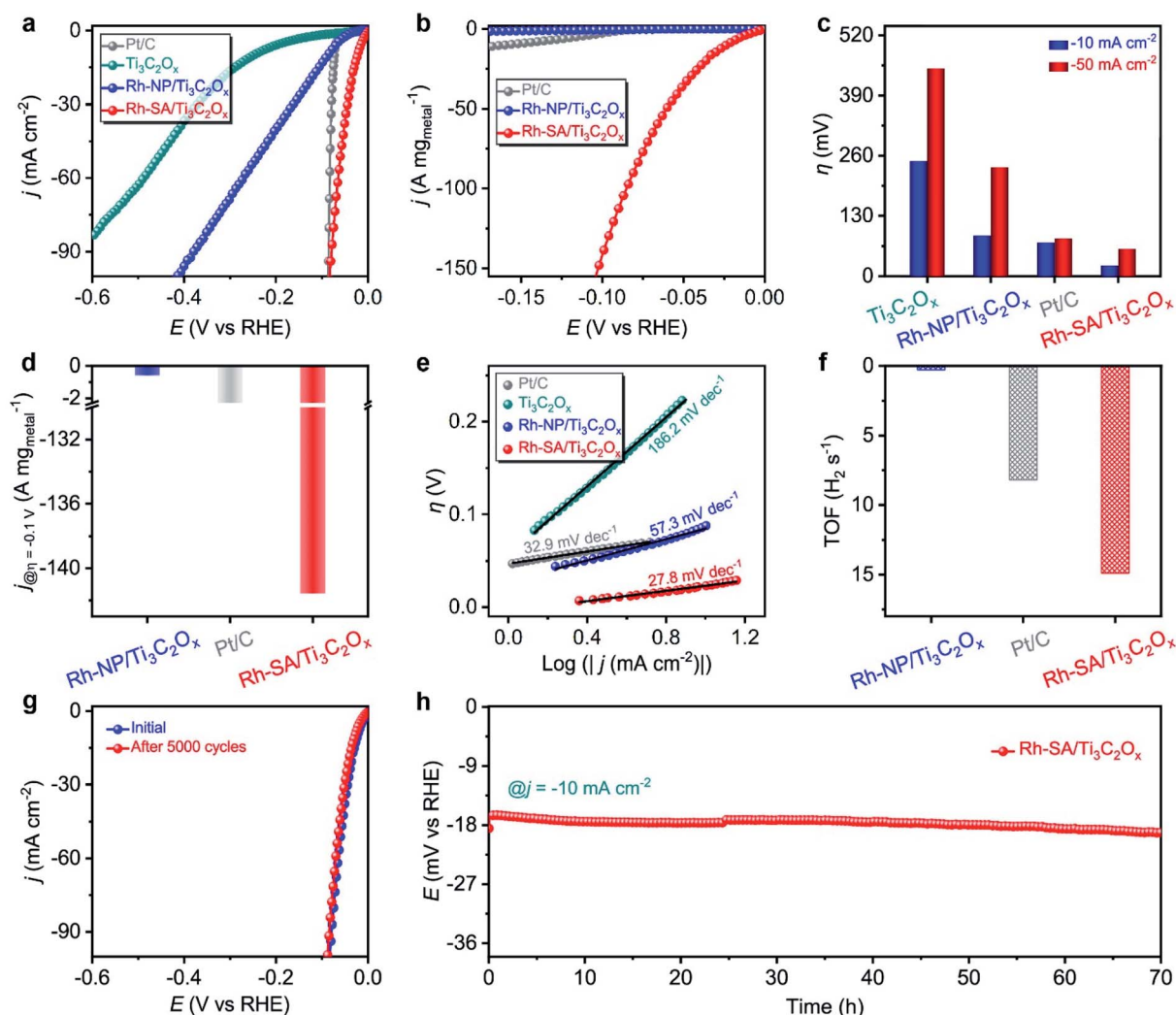


Fig. 2 The HER electrochemical performances of the as-prepared catalysts measured under acidic conditions: (a) the geometric-area-normalized HER polarization curves of  $\text{Ti}_3\text{C}_2\text{O}_x$ , Rh-NP/ $\text{Ti}_3\text{C}_2\text{O}_x$ , Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$ , and commercial Pt/C catalysts in 0.1 M  $\text{H}_2\text{SO}_4$  solution, at a scan rate of  $10 \text{ mV s}^{-1}$ ; (b) the corresponding mass-normalized HER polarization curves; (c) the overpotentials at current densities of  $-10$  and  $-50 \text{ mA cm}^{-2}$ ; (d) the HER mass activity at  $\eta = -0.1 \text{ V}$  vs. RHE; (e) Tafel plots; (f) TOF values at  $\eta = -0.1 \text{ V}$  vs. RHE; (g) polarization curves of the Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$  initially and after 5000 cycles; (h) stability testing of Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$  for the HER at  $j = -10 \text{ mA cm}^{-2}$ .

$\text{Ti}_3\text{C}_2\text{O}_x$  is 248.4 and 52.1 times more active than the Rh-NP/ $\text{Ti}_3\text{C}_2\text{O}_x$  and Pt/C catalysts, respectively.

The rapid rise in current density is also reflected in the dynamic process using Tafel plots, which provide profound insights into the fundamental HER kinetic mechanism that occurs on the surfaces of the electrocatalysts.<sup>38–41</sup> As a result of the low energy barrier (0.44 eV on Pt) of the Volmer step, the kinetic rate-limiting step for the Pt catalyst is the Tafel process, and the theoretical Tafel slope is  $30 \text{ mV dec}^{-1}$  (here the Tafel slope of the commercial Pt catalyst was measured to be  $32.9 \text{ mV dec}^{-1}$ ).<sup>38,42</sup> Remarkably, the Tafel slope of the Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$  catalyst is as low as  $27.8 \text{ mV dec}^{-1}$ , which is far lower than the values of  $57.3 \text{ mV dec}^{-1}$  for Rh-NP/ $\text{Ti}_3\text{C}_2\text{O}_x$  and  $186.2 \text{ mV dec}^{-1}$  for  $\text{Ti}_3\text{C}_2\text{O}_x$ , and highly comparable to those of previously reported electrocatalysts (Table S2†). These results indicate that the electrocatalytic HER kinetics on the Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$  electrocatalyst are determined by the Tafel step rather than a coupled

Volmer–Tafel or Volmer–Heyrovsky process. In other words, the prior Volmer step is significantly accelerated. By extrapolating the Tafel plots to a value of the potential of 0 V, the exchange current density ( $j_0$ ) was determined, which can be applied to assess the kinetic HER activity. As shown in Fig. S8,† the  $j_0$  value of the Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$  catalyst is  $1.57 \text{ mA cm}^{-2}$ , which is much higher than that of Rh-NP/ $\text{Ti}_3\text{C}_2\text{O}_x$  ( $0.33 \text{ mA cm}^{-2}$ ) and those of most previously reported HER electrocatalysts (Table S3†), suggesting a more rapid HER rate and an additional kinetic advantage for Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$ .<sup>43–46</sup> Moreover, compared with Rh-NP/ $\text{Ti}_3\text{C}_2\text{O}_x$ , the HER process of Rh-SA/ $\text{Ti}_3\text{C}_2\text{O}_x$  is favorable, confirming that the enhanced atomic efficiency of the Rh SAs could effectively boost the catalytic activity, even at an extremely low Rh loading. We ascribe this remarkably enhanced HER catalytic activity to the associated interactions between the  $\text{Ti}_3\text{C}_2\text{O}_x$  substrate and the individual Rh SAs.

Turnover frequency (TOF), which is related to the number of  $\text{H}_2$  molecules evolved per second per active site, is the most important figure of merit to use to gain insight into the intrinsic activity of an electrocatalyst.<sup>47–50</sup> Impressively, the TOF number of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> is 14.9 H<sub>2</sub> s<sup>-1</sup> at an overpotential of -0.1 V vs. RHE (Fig. 2f and S9†), which is around 49.7 and 1.8 times greater than those of Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (0.3 H<sub>2</sub> s<sup>-1</sup>) and commercial Pt/C (8.2 H<sub>2</sub> s<sup>-1</sup>), respectively. To gain further insight into the high activity of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst, electrochemical impedance spectroscopy (EIS) and electrochemical active surface area (ECSA) measurements were carried out. As shown in Fig. S10,† the Nyquist plots reveal that Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> exhibits an enhanced electron transfer rate and fast catalytic kinetics, thus leading to excellent electrochemical activity.<sup>51</sup> The value of the double layer capacitance ( $C_{dl}$ ) values of the catalysts were measured to estimate the ECSAs by recording cyclic

voltammetry (CV) cycles at different scan rates (Fig. S11a–c†).<sup>52–55</sup> As displayed in Fig. S11d,† the  $C_{dl}$  of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst is 101.6 mF cm<sup>-2</sup>, which is 7.0 and 1.9 times greater than those of Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (14.5 mF cm<sup>-2</sup>) and Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (52.2 mF cm<sup>-2</sup>), respectively. This implies that Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> has a higher surface area and more exposed active sites than the other catalysts, which are beneficial to enhancing its HER activity. These results are in good agreement with the trends in the Tafel slopes, which further confirms the superiority of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst. Moreover, as the surface topology can affect catalyst performance, the ECSA-normalized current density was also measured to determine the intrinsic HER activity of the catalyst. From the normalization of the current density curves by the ECSA (Fig. S12†), it can be seen that the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst has a non-dominant activity due to its high  $C_{dl}$  value.

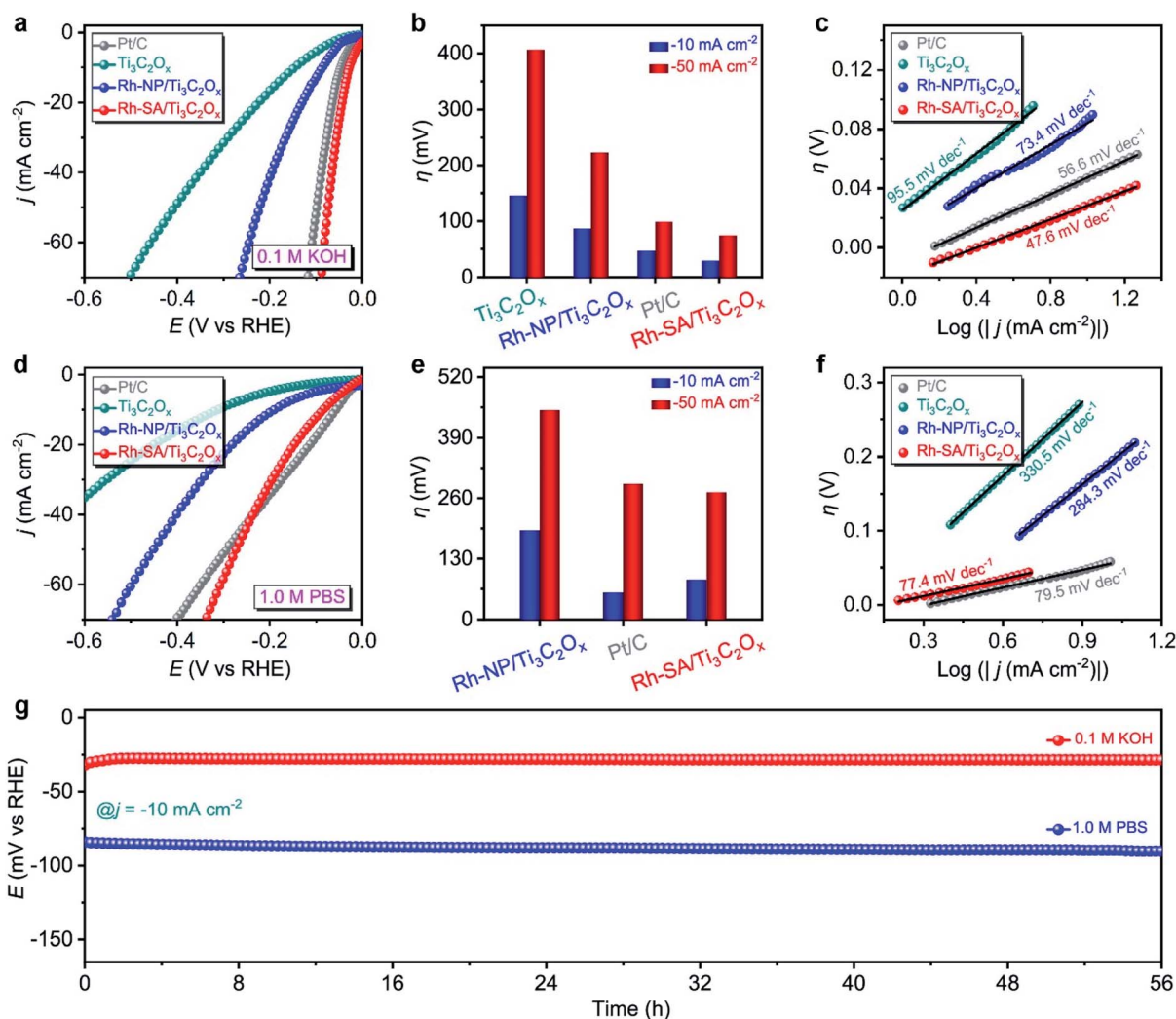


Fig. 3 HER electrochemical performances of the as-prepared catalysts measured under alkaline and neutral conditions: (a) the HER polarization curves of the Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, and commercial Pt/C catalysts measured in 0.1 M KOH solution at a scan rate of 10 mV s<sup>-1</sup>; (b) the overpotentials at various current density and (c) Tafel plots corresponding to (a); (d) the HER polarization curves of Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, and commercial Pt/C catalyst in 1.0 M PBS solution at a scan rate of 10 mV s<sup>-1</sup>; (e) the overpotentials at various current density and (f) Tafel plots corresponding to (d); (g) stability testing of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> towards the HER at  $j = -10$  mA cm<sup>-2</sup> in 0.1 M KOH and 1.0 M PBS solutions, respectively.

Apart from superior electrocatalytic activities, we further examined the long-term stability of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> for practical applications. As shown in Fig. 2g, continuous CV cycling tests of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> were conducted over 5000 cycles. After the cycling tests, the polarization curve revealed no variation in current density from that recorded initially. In addition, chronoamperometric testing performed at a constant overpotential showed almost no decrease in current density over 70 h (Fig. 2h), confirming the reliable stability of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>. No clusters and particles could be observed on the surface of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> nanosheets after the stability testing (Fig. S13<sup>†</sup>),

confirming its robust structural stability during the HER process.

The HER electrochemical performances of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> were also studied under alkaline and neutral conditions. Fig. 3a shows the LSV curves of the as-prepared catalysts in 0.1 M KOH electrolyte. Notably, the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst exhibits excellent performance, with an overpotential of 29 mV to achieve a current density of  $-10 \text{ mA cm}^{-2}$ , surpassing that of Pt/C (47 mV) and most previously synthesized HER electrocatalysts under alkaline conditions (Table S4<sup>†</sup>), much higher than those of Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (146 mV) and Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (97 mV) (Fig. 3b).

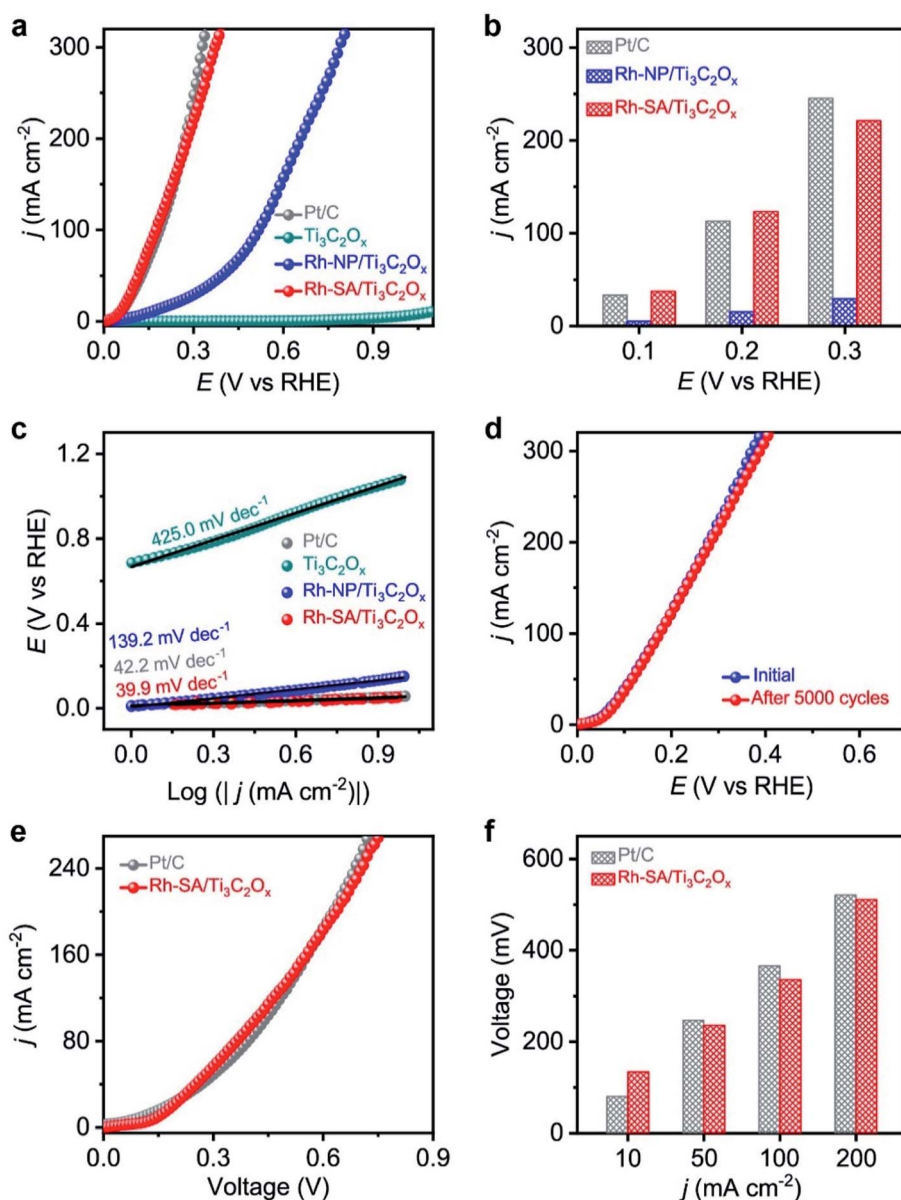


Fig. 4 HzOR and OHZS electrochemical performances of the as-prepared catalysts measured under alkaline conditions: (a) the HzOR polarization curves of the Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, and commercial Pt/C catalysts measured in 1.0 M KOH + 0.1 M N<sub>2</sub>H<sub>4</sub> solution at a scan rate of 10 mV s<sup>-1</sup>; (b) the current densities at various potentials; (c) the corresponding Tafel plots; (d) HzOR polarization curves of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> initially and after 5000 cycles; (e) OHZS polarization curves in 1.0 M KOH + 0.1 M N<sub>2</sub>H<sub>4</sub> solution using Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> and commercial Pt/C as both the anode and cathode; (f) the voltages required to reach different current densities for OHZS.

Meanwhile, Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> also presents excellent HER performance at high current densities in alkaline solution, as shown in Fig. 3b. Fig. 3c shows that Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> exhibits the fastest dynamics, with a Tafel slope of 47.6 mV dec<sup>-1</sup>, surpassing the performance of Pt/C of 56.6 mV dec<sup>-1</sup>, and much faster than those of Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (95.5 mV dec<sup>-1</sup>) and Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (73.4 mV dec<sup>-1</sup>).

In 1.0 M PBS electrolyte (Fig. 3c), Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> only requires an overpotential of 85 mV to achieve a current density of -10 mA cm<sup>-2</sup>, which is close to the performance of commercial Pt/C (57 mV) and 2.2 times lower than of Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (191 mV), while Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> exhibits almost no activity (Fig. 3d and e). The Tafel slope is 77.4 mV dec<sup>-1</sup> for Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, as displayed in Fig. 3f, which is much lower than those of Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (330.5 mV dec<sup>-1</sup>) and Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (284.3 mV dec<sup>-1</sup>), and even those of commercial Pt/C (79.5 mV dec<sup>-1</sup>) and most previously synthesized HER electrocatalysts under neutral conditions (Table S5<sup>†</sup>). In addition, the chronoamperometry testing demonstrated that the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst works efficiently for more than 56 h in 0.1 M KOH and 1.0 M PBS electrolytes (Fig. 3g), respectively. These results strongly

demonstrate that the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst shows unparalleled advantages as a superior pH-universal electrocatalyst for the electrochemical HER among the best recently reported HER electrocatalysts (Tables S2, S4, and S5<sup>†</sup>).

### Evaluation of the HzOR performance

The electrocatalytic HzOR performance was evaluated in a typical three-electrode configuration with Hg/HgO as the reference electrode, graphite rod as the counter electrode, and 1.0 M KOH + 0.1 M N<sub>2</sub>H<sub>4</sub> solution as the electrolyte. Fig. 4a displays a comparison of the LSV curves of HzOR for the Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, and commercial Pt/C catalysts, which intuitively indicate the much better electrocatalytic activity of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> compared with the other catalysts, and there is no oxidation current in the measured potential window of 0 to 1.1 V vs. RHE when the electrolyte is an aqueous solution of 1.0 M KOH + 0.1 M N<sub>2</sub>H<sub>4</sub>.

Specifically, Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> achieves large anodic current densities of 37.5, 123.1, and 221.4 mA cm<sup>-2</sup> at working potentials of 0.1, 0.2, and 0.3 V vs. RHE (Fig. 4b), respectively, which are far superior to those of Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> and very close to

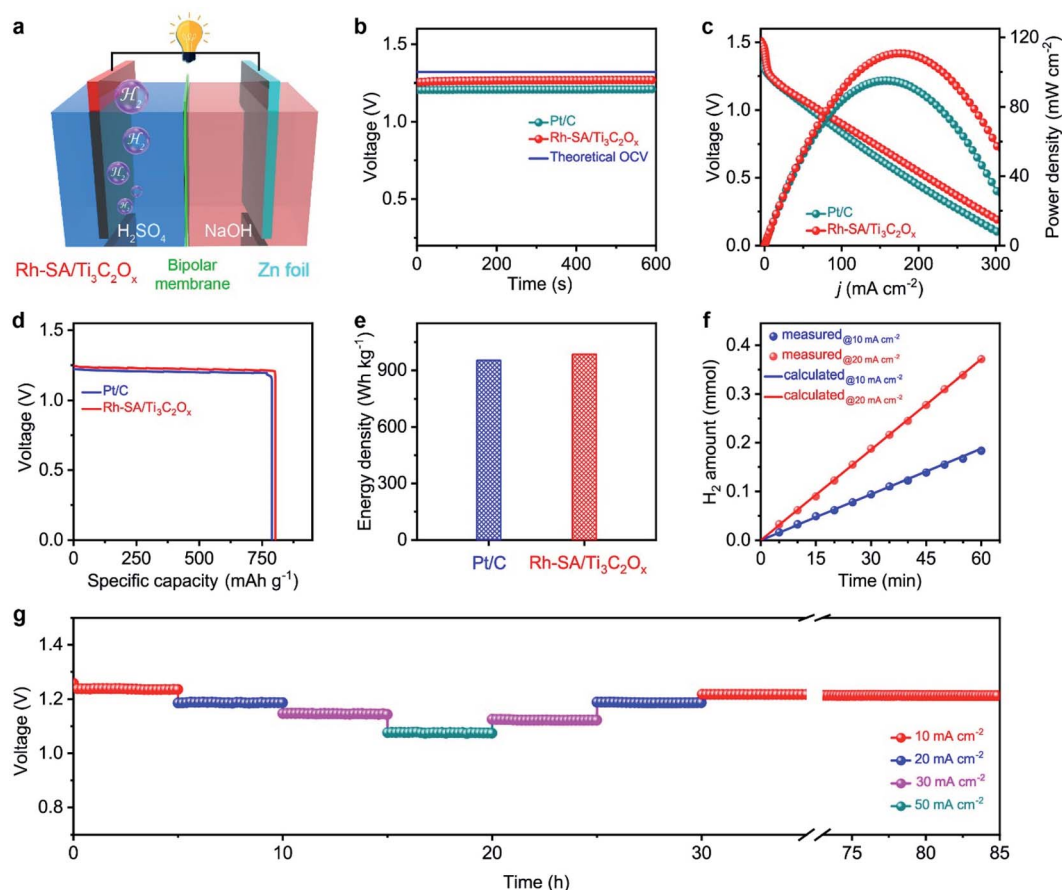


Fig. 5 Zn-H<sub>2</sub> battery hydrogen production system: (a) schematic illustration of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>-based Zn-H<sub>2</sub> battery hydrogen production system; (b) the open-circuit voltage curves; (c) the polarization curves and the corresponding power densities; (d) the plots of voltage versus specific capacity at a scan rate of 10 mA cm<sup>-2</sup>, where the specific capacity was normalized to the mass of consumed Zn; (e) plots of energy densities; (f) the amount of generated H<sub>2</sub> as a function of the reaction time at current densities of 10 and 20 mA cm<sup>-2</sup>, respectively; (g) discharge curves of the hydrogen production system based on Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> with current densities from 10 to 50 mA cm<sup>-2</sup> and the long-term stability tests at current densities of 10 mA cm<sup>-2</sup> over 55 h.

those of commercial Pt/C. Also, Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> outperforms most of the previously reported HzOR electrocatalysts (Table S6†). The corresponding Tafel plots (Fig. 4c) indicate that the Tafel slope of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> is only 39.9 mV dec<sup>-1</sup>, which is much lower than those of Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (425.0 mV dec<sup>-1</sup>) and Rh-NP/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> (139.3 mV dec<sup>-1</sup>) and even surpasses that of commercial Pt/C (42.2 mV dec<sup>-1</sup>), suggesting that it exhibits the most favorable catalytic kinetics towards the HzOR. As one of the critical factors for practical applications, the durability of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> was then evaluated by carrying out successive CV tests. As shown in Fig. 4d, the HzOR activity of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst was well retained, showing negligible decay after 5000 potential cycles, demonstrating its excellent stability. In addition, a control experiment was performed (Fig. S14†), confirming that the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst cannot catalyze the direct decomposition of hydrazine in alkaline solution.<sup>56–58</sup>

Encouraged by the high activities and stabilities of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> nanosheets towards the HER and HzOR, we further investigated their application as an OHZS electrocatalyst, used bifunctionally as an cathode and anode in a two-electrode electrolyzer. Fig. 4e shows the LSV curves of the OHZS of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> and commercial Pt/C, in which enhanced energy efficiency can be seen using hydrazine oxidation to assist H<sub>2</sub> production.<sup>59–61</sup> Specifically, potentials of only 134, 236, 336, and 511 mV were required in this OHZS system to reach current densities of 10, 50, 100, and 200 mA cm<sup>-2</sup> V (Fig. 4f), respectively, which are much closer to the values of Pt/C (80, 247, 366, and 521 mV).

### Evaluation of Zn–H<sub>2</sub> battery performance

Considering the highly efficient HER catalytic activity of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst, a Zn–H<sub>2</sub> battery hydrogen production

system was constructed. As illustrated in Fig. 5a, this system was assembled using carbon paper supported Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> as the cathode, Zn plate as the anode, and 2.0 M H<sub>2</sub>SO<sub>4</sub> and 4.0 M NaOH as the catholyte and anolyte, respectively. A bipolar membrane (BPM) was used as a separator for preventing bulk neutralization of the acidic catholyte and alkaline anolyte. For comparison, the commercial 20 wt% Pt/C catalyst was also measured under the same conditions. As expected, Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> provides a stable open-circuit voltage (OCV) of 1.26 V for the sole hydrogen production system, which is higher than that of Pt/C (1.21 V) and close to that of the theoretical value (1.32 V, the calculation details of which can be found in the ESI† file). The discharge polarization curves and the corresponding power density curves are depicted in Fig. 5c. As shown, the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst delivers a higher peak power density of 110.8 mW cm<sup>-2</sup> at 175 mA cm<sup>-2</sup>, much better than that of Pt/C of 95.1 mW cm<sup>-2</sup> at 156.5 mA cm<sup>-2</sup>. Moreover, the specific capacity over Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> reaches 802.4 mA h g<sub>Zn</sub><sup>-1</sup> at a current density of 10 mA cm<sup>-2</sup> on the basis of consumed Zn mass (Fig. 5d), corresponding to an energy density of 985.2 W h kg<sub>Zn</sub><sup>-1</sup> (close to the theoretical value of 1082.4 W h kg<sub>Zn</sub><sup>-1</sup>, see the calculation details in the ESI† file), which surpasses those of Pt/C (786.6 mA h g<sub>Zn</sub><sup>-1</sup>; 952.8 W h kg<sub>Zn</sub><sup>-1</sup>).

To testify the hydrogen-production efficiency of this system, the volumes of hydrogen produced upon the discharge process were recorded *via* the drainage gas collection method (Fig. S15†).<sup>62,63</sup> The measured hydrogen yield fitted well to those of the theoretical calculations, thus the Faradaic efficiency (FE) was measured to be closed to 100% for H<sub>2</sub> generation (Fig. 5f). Fig. 5g shows the high stability of the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> for around 5 h at various discharge current densities from 10 to 50 mA

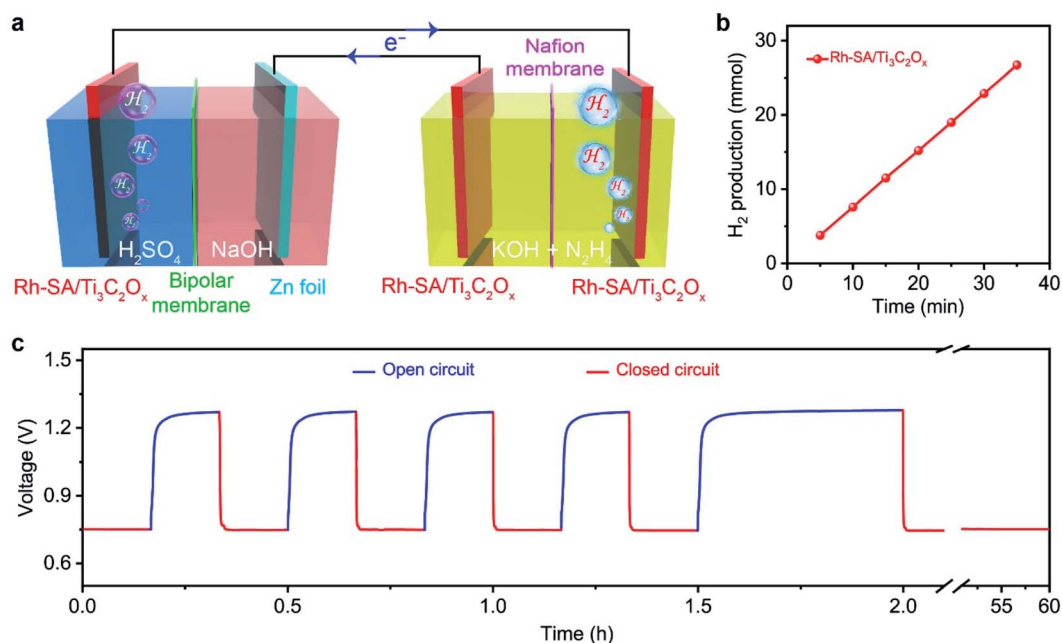


Fig. 6 Self-driven dual hydrogen production system: (a) schematic illustration of the dual hydrogen production system self-driven by the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst; (b) the total amount of generated H<sub>2</sub> as a function of the reaction time for this self-driven dual hydrogen production system; (c) the long-time voltage curve of the system at closed/open circuit.



$\text{cm}^{-2}$ . In particular, the voltage shows almost no decay after the long-term stability tests at a current density of  $10 \text{ mA cm}^{-2}$  over 55 h, indicating its robust long-term discharging capability.

### Evaluation of the self-driven dual hydrogen production system performance

Based on the successful assembly of the Zn–H<sub>2</sub> battery and the excellent bifunctional catalytic activity of Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> discussed above, a self-driven dual hydrogen production system was constructed. As illustrated in Fig. 6a, the self-driven dual hydrogen production system consists of the integration of a Zn–H<sub>2</sub> battery using an Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> cathode and Zn plate as the anode to drive the OHzS for H<sub>2</sub> production (Fig. S16†). In this

system, H<sub>2</sub> is generated simultaneously *via* two pathways: the cathode of the Zn–H<sub>2</sub> unit and the cathode of the OHzS. As shown in Fig. 6b, the total amount of hydrogen produced was collected. Based on the linear relationship between the H<sub>2</sub> yield and the elapsed time, the H<sub>2</sub> production rate was calculated as  $45.77 \text{ mmol h}^{-1}$ , which outperforms the reported values of self-driven H<sub>2</sub> production systems (Table S7†), demonstrating the exciting potential of this system for highly efficient H<sub>2</sub> production. As shown in Fig. 6c, the voltage–time curve exhibits that this system can stably output a voltage of 0.75 V when the circuit is closed, as well as an open-circuit voltage of 1.27 V when the device is in an open circuit. Impressively, stable output voltage can be supplied over 58 h without obvious decay,

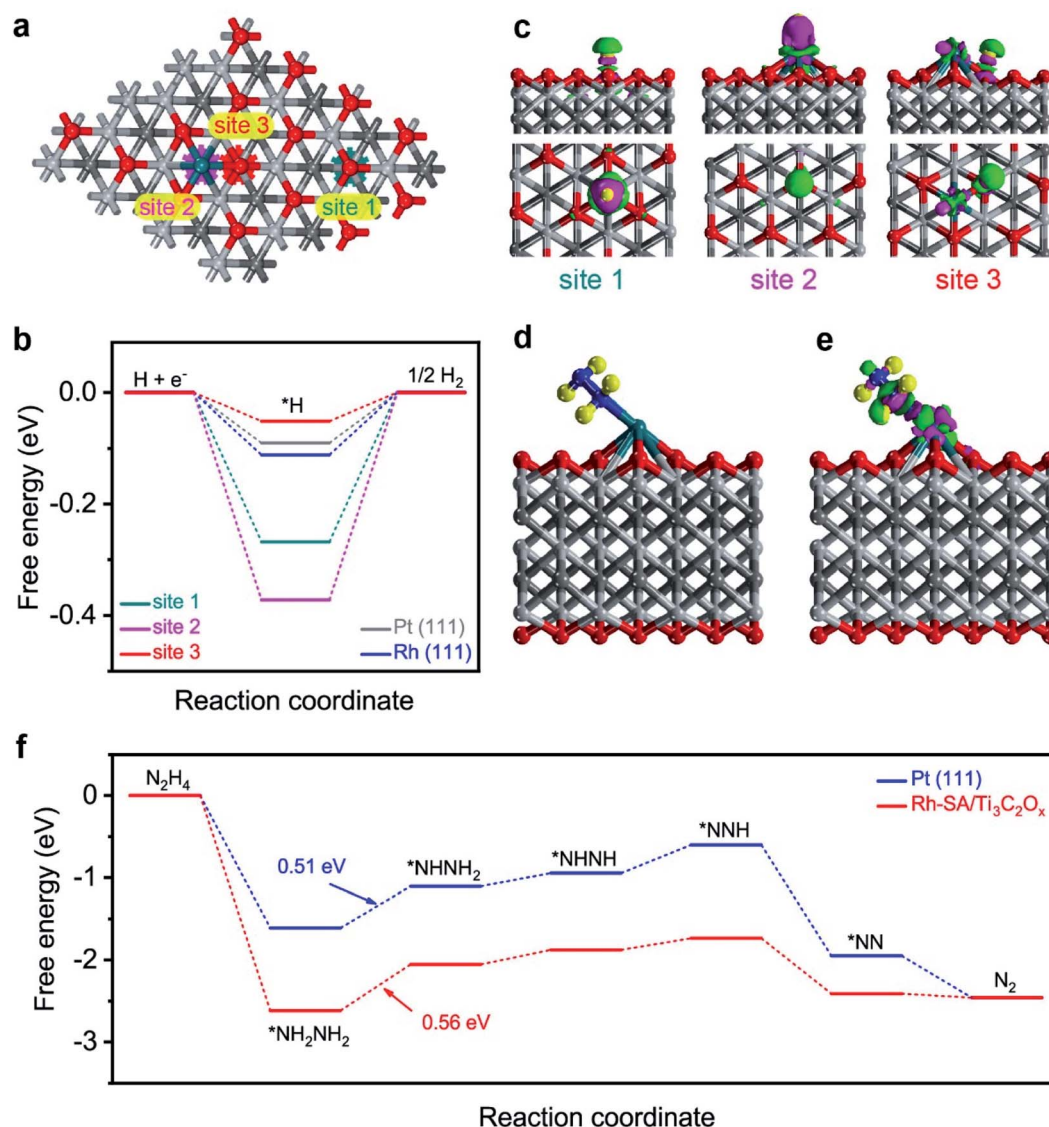


Fig. 7 First-principles calculations of the HER and HzOR: (a) the three different sites over the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst surface: 1, O, 2, Rh, and 3 Rh–O sites; (b) free-energy profiles of the HER on the different sites over the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>, Pt(111), and Rh(111) surfaces; (c) side- and top-view of the three-dimensional charge density difference of the H-adsorbed configuration on the different sites over the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst surface, where the pink and green regions represent charge depletion and accumulation in the space, respectively; (d) optimized atomic structure model and (e) the charge density difference of the N<sub>2</sub>H<sub>4</sub>-adsorbed configuration on the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> catalyst; (f) free-energy profiles of the HzOR on the Rh-SA/Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub> and Pt(111) surfaces.



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