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# Synthesis of noble metal nanoarrays via agglomeration and metallurgy for acidic water electrolysis

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Noble metal electrocatalysts remain the mainstay for proton exchange membrane water electrolysis, majorly due to their exceptional activity and durability in acidic media. However, conventional powder and particle catalysts intensively suffer from aggregation, shedding and poor electron conductivity in practical applications. Here, we develop a micellar brush-guided method to agglomerate and smelt metal nanoparticles into erect nanoarrays with designable constitutions on various substrates. While the nanoarrays of stacked nanoparticles show poor stability in the acidic media, the smelting treatment substantially enhances the electron conductivity by more than four order of magnitude and reinforces the nanoarray architectures. This allows the tailored fabrication of self-supported acid-durable metallic and alloy nanoarray catalysts with outstanding hydrogen evolution activity, and metal oxide nanoarray and RuO<sub>x</sub>- nanoarray in a proton exchange membrane electrolyzer further enables a long-term stable water electrolysis process for more than 500 h at 1 A cm<sup>-2</sup>.

Hydrogen (H<sub>2</sub>) production from electrolysis of water using renewable electricity is widely recognized as a sustainable alternative to polluting fossil fuels<sup>1-3</sup>. The proton exchange membrane (PEM) water electrolysis technology, featured with scalability, high current density and superior power regulation compared to the dominant alkaline water electrolysis technology<sup>4-7</sup>, is well-suited to the volatility of renewable electricity from wind, light, water wave, etc. However, the PEM water electrolysis is performed in an acidic environment, which remarkably limits the choice of electrocatalysts<sup>8-10</sup>. The noble metal electrocatalysts remain the major choice for the anode (e.g. IrO2 and RuO2 powder) and the cathode (e.g. Pt/C powder) catalysts in acidic water electrolysis mainly due to their remarkable durability<sup>11-13</sup>. Nevertheless, these powder and particle catalysts are normally bonded onto the membrane or diffusion electrodes (e.g. carbon cloth/paper, Ti fiber felt) for PEM devices through adhesives, which inevitably leads to problems such as active site burial, catalyst shedding and poor electron conductivity, especially at a high current density<sup>14</sup>.

Metal nanoarrays with appealing features such as free-standing architecture<sup>15-17</sup>, open space, fast charge transfer, and low interfacial barriers<sup>18-21</sup> are highly useful for catalysis<sup>22</sup>, sensors<sup>23</sup> and optoelectronics<sup>24</sup>. For transition metals (e.g. Fe, Co, Ni, Cu, Ti), they can normally be grown into corresponding hydroxide nanoarrays on electrodes by hydro/solvothermal processes<sup>25</sup>. The nanoarray electrodes are more conducive to active site exposure, mass transfer and electrolyte wetting, which significantly improve the activity and stability of the electrocatalysts compared to those in powder form<sup>14,18,26,27</sup>. However, limited by the intrinsic chemical properties and engineering difficulties, the growth of self-supported noble metal nanoarrays on electrodes has rarely been reported. Methods of casting or doping noble metals onto supported nanoarrays (e.g. TiO<sub>2</sub> nanoarrays) have been proposed to allow noble metals to take advantage of nanoarray architectures<sup>28,29</sup>. Nevertheless, these frequently suffer from low efficiency, low noble metal density, as well as the limited choice and moderate electron conductivity of supported nanoarrays. It remains a

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critical challenge to precisely and rapidly agglomerate metal species on desired substrates to form self-supported vertically aligned architectures with sufficient catalytic interfaces.

Here, we develop a micellar brush-guided method to regulate the agglomeration of metal NPs to form erect nanoarrays on desired substrates. The highly solvated corona of the soft template also favors a simultaneous penetration of two or more metal NPs, leading to the formation of hybrid nanoarrays. These densely stacked metal NPs are further smelted at high temperatures to produce continuous metallic, alloy and metal oxide nanoarrays, exhibiting enhanced the electron conductivity by more than four order of magnitude and reinforced structures. When applied to the cathode and anode of a PEM water electrolysis device, these self-supported noble metal nanoarray electrocatalysts considerably boost the hydrogen and oxygen evolution reactions, and show sustainably durability at an industrial-level current density for more than 500 h at 1 A cm<sup>-2</sup>.

#### **Results and discussion**

#### Agglomeration of metal NPs into nanowires

It has been previously found that a diverse array of metal NPs tend to associate with the poly(2-vinylpydidine) (P2VP) corona of the micellar brushes formed by PFS-*b*-P2VP [PFS = poly(ferrocenyldimethylsilane)] through coordination interactions<sup>30,31</sup>. However, the metal NPs were

deposited on the micellar brushes majorly in a rather sparse manner, which was far from the self-supported nanoarrays. In consideration of the factor that the average distance between the P2VP corona chains in the cylindrical micelles of PFS-*b*-P2VP is *ca*. 3.5 nm<sup>32</sup>, ideally, metal NPs with matched size would be more preferrable to fill the coronal gaps, aiming at a higher loading density. To this end, we prepared a series of metal (Ru, Ir, Rh, Pt) NPs with precisely controlled diameters ranging from 1.2 to 3.4 nm, which were stabilized by adsorbed anions (acetate) in ethylene glycol (Supplementary Fig. 1).

Ru NPs with an average diameter of 3.3 nm were first employed to interact with the cylindrical micelles formed by PFS<sub>29</sub>-*b*-P2VP<sub>230</sub> (the subscripts refer to the degree of polymerization of each block, Supplementary Fig. 2) in ethylene glycol. After being mixed for 10 min, the Ru NPs were predominantly concentrated in the periphery of the P2VP corona (Fig. 1A). Subsequently, the Ru NPs gradually penetrated into the inner corona and eventually occupied the entire corona layer. The average spacing between the adjacent Ru NPs decreased from  $5.1 \pm 1.9$ to  $0.5 \pm 0.08$  nm during the agglomeration process (Supplementary Fig. 3). This led to the formation of regular nanowires with smooth contours and tightly stacked Ru NPs (Fig. 1B). X-ray photoelectron spectroscopy (XPS) showed that the Ru NPs were bonded to the pyridine groups in the P2VP corona mainly through coordination interactions, and the Ru-N association increased with the agglomeration





spectrometric (EDS) mapping images of a resulting nanowire with tightly packed Ru NPs. **C** XPS spectra of N 1*s* for nanowires sampled at different stages during the agglomeration process. **D** Schemes illustrate the dynamic coordination between Ru NPs and pyridine groups in the P2VP corona, which leads to a chain-like stacking of Ru NPs. period (Fig. 1C). It seemed that the coordination between the metal NPs and the pyridine groups in the P2VP corona was relatively reversible and dynamic. During the agglomeration process, the adjacent P2VP chains with a gap of 3.5 nm were constrained by the pre-loaded Ru NPs, and other Ru NPs were temporarily prevented from penetrating into the inner corona laver (Fig. 1D left). However, the reversible and dynamic coordination promoted the sequential migration of the Ru NPs (Fig. 1D middle), which ultimately led to a dense and linear stacking of metal NPs in the gaps of P2VP chains (Fig. 1D right). Thus, in some regions, the Ru NPs were found to stack in a chain-like fashion along the corona chains (Supplementary Fig. 4). Notably, the agglomeration of Ru NPs was highly dependent on the concentration of the acetate ( $c_{acetate}$ , Supplementary Fig. 5). Ru NPs with smaller diameters of 2.1 and 1.2 nm were also employed to interact with the cylindrical micelles, which revealed less tight stacking and relatively random distribution in the resulting nanowires (Supplementary Fig. 6). The cylindrical micelles also successfully templated the dense agglomeration of Ir, Rh and Pt, NPs with average diameters of ca. 3.0 nm to form regularly shaped nanowires (Supplementary Fig. 7).

To gain more insights into the agglomeration of metal NPs, we successively and simultaneously added Ru and Pt NPs with comparable sizes into the solution of PFS<sub>29</sub>-*b*-P2VP<sub>230</sub> cylindrical micelles. In terms of the relatively larger Ru (3.3 nm) and Pt NPs (3.4 nm), the first added Ru NPs that originally located in the outer layers of the P2VP corona migrated to the inner space after the sequential addition of Pt NPs (Supplementary Fig. 8A). The pre-loaded Ru NPs prevented the further added Pt NPs from penetrating into the inner corona layer, and thus the latter eventually majorly distributed in the periphery of the resulting nanowire. When the Ru and Pt NPs were simultaneously added, they both uniformly deposited in the corona of the micelles, forming hybrid nanowires (Supplementary Fig. 8B). Regarding the smaller Ru (1.2 nm) and Pt NPs (1.6 nm), the sequential and simultaneous addition of the two metal NPs solely led to the formation of hybrid nanowires with randomly distributed Ru and Pt NPs (Supplementary Fig. 9). Apparently, the pre-deposited small Ru NPs were unable to hinder the diffusion and immobilization of the later added Pt NPs. Preliminary molecular dynamics calculation showed that the association between the metal NPs and the P2VP corona is thermodynamically favored, and the metal NPs with comparable size with the gap of corona chains reveal high affinity with the P2VP corona (Supplementary Fig. 10).

#### Agglomeration of metal NPs into erect nanoarrays

Micellar brushes were subsequently prepared on desired substrates (e.g. carbon cloth) via living crystallization-driven self-assembly initiated by the pre-immobilized micelle seeds (Supplementary Fig. 11) to direct the agglomeration of metal NPs (Fig. 2A). Upon placing the micellar brush-decorated carbon cloth, the solution of Ru NPs (3.3 nm,  $c_{\text{acetate}} = 0.015 \text{ mol L}^{-1}$ ) quickly turned from dark brown to light brownish, indicating an efficient agglomeration process (Fig. 2B). The loading of Ru NPs on the carbon cloth increased with the immersion cycles and eventually reached *ca*.  $0.22 \text{ mg cm}^{-2}$ . Scanning electron microscopy (SEM) images showed that all of the exposed surfaces were completely covered by densely and vertically aligned nanoarrays (Fig. 2C, D, Supplementary Fig. 12), which were solely comprised by tightly stacked Ru NPs (Supplementary Fig. 13). The height of such Ru NPs-nanoarrays can be precisely adjusted in a range of ca. 0.5-1.6 µm by the amount of unimers added during the surface-initiated living growth of the micellar brush templates (Supplementary Fig. 14). Nanoarrays of binary metal NPs (RuPt) or quaternary metal NPs (RulrRhPt) were also fabricated following a similar agglomeration process (Supplementary Fig. 15).

The electrical conductivity of the metal NPs-nanoarrays on conductive titanium sheets was then evaluated by conductive atomic force microscopy, where the conductive probe was placed on the top of an individual nanowire (Fig. 2E), allowing the detection of electron conductivity along the longitudinal direction. While the PFS<sub>29</sub>-*b*-P2VP<sub>230</sub> micellar brushes on the titanium sheet were absolutely insulative, the nanoarrays with higher loading of Ru NPs that obtained by decreased concentration of acetate showed ascending ohmic responses (Fig. 2F). The corresponding nonlinear current-voltage (*I–V*) curves illustrated a featured electron tunneling between the nanoparticle islands<sup>33</sup>. The closer stacking of Ru NPs allowed a shorter and less hindered electron conduction path, which substantially boosted the electron conductivity. The optimal electron conductivity of Ru NPs-nanoarray was calculated to be 2.9 S m<sup>-1</sup> at a high bias voltage region ( $2.5 \le V \le 4.0$ ), which was in line with conventional semiconducting materials.

# Fabrication of continuous metallic and alloy nanoarrays by smelting

Insulating barriers including organic templates and voids are inevitable in assemblies of metal NPs, and critically limit the electron conductivity. Thus, we aimed to eliminate the insulative templates and the interparticle voids by smelting the metal NPs-nanoarray at high temperatures (Fig. 3A). This was favored by the lower melting temperature of metal NPs than that of the bulk counterpart<sup>34</sup>. To this end, we smelted the Ru NPs-nanoarray in an inert atmosphere (N<sub>2</sub>) at high temperatures (T). While a high temperature (800 °C) destroyed the nanoarray architectures (Supplementary Fig. 16), the Ru NPsnanoarrays treated at relatively lower temperatures (400-600 °C) integrally maintained the nanoarray architecture (Fig. 3B, Supplementary Fig. 17). The interparticle voids were hardly observed upon increasing the smelting temperature to 600 °C and the stacked Ru NPs were entirely converted into fused continuous phases without losing the nanowire shapes (Fig. 3C). A similar evolution process was also observed under in situ TEM (Supplementary Fig. 18). The corresponding selected area electron diffraction images transformed from a diffuse ring to a clear dot matrix pattern, suggesting the transition from nanoparticle agglomerates to a highly crystalline structure.

High-resolution TEM (HRTEM) images further revealed that the stacked Ru NPs fused into interconnected polycrystalline grains (Supplementary Fig. 19), and eventually formed a continuous crystalline morphology (Fig. 3D). Atomic-scale HRTEM image further revealed the presence of abundant atomic vacancies that linearly distributed along the grain boundaries (GBs) in Ru-nanoarray-600 (Supplementary Fig. 20A). The lattice space along the GB was measured to be 0.46 nm, nearly twice the value of other regions (0.24 nm), confirming the loss of atomic layer (Supplementary Fig. 20B). X-ray diffraction (XRD) analysis of metallic Ru-nanoarray-600 presented sharp diffraction peaks, corresponding to a typical hexagonally close-packed (hcp) structure for Ru crystals (Fig. 3E). Extended X-ray absorption fine structure (EXAFS) spectra of Ru-nanoarray-600 showed that the bond length of the first shell Ru-Ru was red-shifted by 0.02 Å compared to that of Ru foil, probably due to the vacancies (Supplementary Fig. 20C). Such lengthened Ru-Ru bonds suggested that the atomic vacancies in metallic Ru-nanoarrays would be able to tune the covalency and electronic structures.

The resulting continuous metallic nanoarrays revealed fairly linear *FV* curves throughout the full bias voltage region ( $-0.4 \le V \le 0.4$ ) along the longitudinal direction (Fig. 3F). A relatively low bias voltage of 0.4 V gave a current of microampere level, while the nanoarray of stacked Ru NPs failed to be activated (Fig. 2F). Apparently, the elimination of the insulative templates and the interparticle voids, and the subsequent creation of continuous metallic conductive paths substantially enhanced the electron conductivity. Remarkably, the electron conductivity of the metallic Ru-nanoarray-600 reached  $3.1 \times 10^4$  S m<sup>-1</sup> in the longitudinal direction, which was four orders of magnitude higher than that of the Ru NPs-nanoarray. The generation of a continuous monocrystalline phase was undoubtably beneficial to the electron conduction.



Fig. 2 | Agglomeration of Ru NPs into erect nanoarrays on desired substrates. A Schematic illustration for the fabrication of Ru NPs-nanoarray on carbon cloth. B Dependence of mass loading of Ru NPs on the immersion cycles. The inset photos show the color change of the solution of Ru NPs upon placing a piece of micellar brush-decorated carbon cloth. **C**, **D** SEM images of the Ru NPs-nanoarray on carbon cloth. The insets show a photo of a piece of carbon cloth covered by the Ru NPs-

nanoarray and a TEM image of a nanowire of the nanoarray constituted by tightly stacked Ru NPs. **E** Schematic illustration of the electron conducting path in the Ru NPs-nanoarray along the longitudinal direction. **F** Electron conduction measurements of Ru NPs-nanoarray obtained at different concentrations of acetate. The inset shows a cross-section SEM image of the Ru NPs-nanoarray on a conductive titanium sheet.

Other metal (Ir, Rh, Pt) NPs-nanoarrays were also facilely converted into continuous metallic nanoarrays by smelting (Supplementary Figs. 21–23). Moreover, binary alloy RuPt-nanoarrays (Fig. 4A–D, Supplementary Fig. 24) and quaternary alloy RuIrRhPt-nanoarrays (Fig. 4E, F, Supplementary Fig. 25) were fabricated as well by smelting the corresponding hybrid metal NPs-nanoarray at 600 °C. STEM-EDS mapping images demonstrated a uniform distribution of the constituent elements. High-resolution HAADF-STEM images and XRD analyses further revealed that the alloy phases were highly crystalline and adopted a face-centered cubic (fcc) structure. Obviously, the smelting allowed the coalescence of various metal NPs and the further cocrystallization into an alloy phase. Noteworthy, when smelting at 400 °C, the dual metal (Ru, Pt) NPs-nanoarray was converted to a heterogeneous hybrid, where Pt nanocrystals were randomly embedded on the metallic Ru-nanoarray (Supplementary Fig. 26).

**Fabrication of continuous metal oxide nanoarrays by smelting** To fabricate the oxide nanoarrays, initially, the Ru NPs nanoarray was directly smelted in air at high temperatures. Despite holding the nanoarray architectures, the Ru NPs were oxidized to stacked RuO<sub>x</sub> NPs (labeled as RuO<sub>x</sub> NPs-nanoarray) with the presence of a large number of dislodged species (Supplementary Fig. 27). It seemed that the oxidation of the Ru NPs prevented the further fusion<sup>35</sup>. Subsequently, we smelted the Ru NPs-nanoarray in a nitrogen/oxygen mixture (N<sub>2</sub>/O<sub>2</sub> = 99/1, v/v) at high temperatures. The decelerated oxidization of the stacked Ru NPs eventually enabled the formation of



**Fig. 3** | **Metallurgy of Ru NPs-nanoarrays into continuous metallic nanoarrays. A** Schematic illustration of the conversion of Ru NPs-nanoarray into continuous metallic Ru-nanoarray-*T* (*T* = 400, 500, 600 °C) by smelting. **B** SEM image of a continuous metallic Ru-nanoarray obtained after smelting at 600 °C (*i.e.* Ru-nanoarray-600). **C** TEM images of Ru NPs-nanoarray and metallic Ru-nanoarray-*T*.

**D** High-resolution TEM images of the boxed areas in **C**. **E** XRD patterns of Ru NPsnanoarray and metallic Ru-nanoarray-600. **F** Electron conduction measurements of metallic Ru-nanoarray-**T**. The inset shows the schematic illustration of the electron conduction measurements and the electron conductive paths.

erect nanoarray of tightly fused  $RuO_x$  crystal grains with a characteristic lattice space of 0.32 nm, corresponding to the (110) plane of  $RuO_2$ (Fig. 4B, Supplementary Fig. 28). The low oxygen atmosphere not only favored the simultaneous fusion and oxidization of Ru NPs, but also provides a feasible access to oxygen vacancies (Supplementary Fig. 29).

#### Electrocatalytic performance of smelted nanoarrays

In consideration of the highly open space and the prominent charge transporting features, as well as the direct decoration on current

collectors, we further evaluated the potential utilization of the smelted nanoarrays in electrocatalysis. As a proof of concept, we chose the metallic and alloy nanoarrays as the catalysts for hydrogen evolution reaction (HER) and the metal oxide nanoarrays for oxygen evolution reaction (OER).

In HER, compared to the carbon cloth decorated with commercial 20 wt% Pt/C or Ru NPs-aggregation (Supplementary Fig. 30), the nanoarray catalysts could achieve a high current density of  $1 \, \text{A cm}^{-2}$  more readily (Fig. 5A, B). The metallic Ru-nanoarray-600 revealed a considerably low overpotential of 82.1 mV at  $1 \, \text{A cm}^{-2}$  and fast reaction



**Fig. 4** | **Metallurgy of hybrid metal NPs-nanoarrays into alloy nanoarrays. A** Schematic illustration of the conversion of (Ru, Pt) NPs-nanoarray to alloy RuPtnanoarray. **B**, **C** SEM and high-resolution HAADF-STEM images of the resulting alloy RuPt-nanoarray. **D** HAADF-STEM and EDS mapping images of the alloy RuPt-

nanoarray with homogeneous distribution of Ru, Pt elements. **E** Schematic illustration of the conversion of (Ru, Ir, Rh, Pt) NPs-nanoarray into alloy RuIrRhPtnanoarray. **F** HAADF-STEM and EDS mapping images of the alloy RuIrRhPtnanoarray with homogeneous distribution of Ru, Ir, Rh, Pt elements.

kinetics of 18.6 mV dec<sup>-1</sup>, much lower than that of Ru NPs-nanoarray (302 mV, 85.8 mV dec<sup>-1</sup>). The alloy RuPt-nanoarray showed a lower overpotential of 73.1 mV at 1 A cm<sup>-2</sup> than metallic Ru-nanoarray-600, probably due to the more diverse electronic structures and synergistic active centers. The electrochemical double-layer capacitance ( $C_{dl}$ ) and the calculated electrochemically active surface area (ECSA) of the nanoarray catalysts were significantly higher than those of the Ru NPs (Supplementary Fig. 31). In particular, the metallic Ru-nanoarray-600 possessed the highest C<sub>dl</sub> and ECSA, more than five folds than that of Ru NPs-aggregation (Supplementary Table 1). The Ru-nanoarray-600 and RuPt-nanoarray demonstrate notable mass activity of 2088 A  $g_{Ru}^{-1}$ and 4267 A  $g_{\text{RuPt}}^{-1}$  respectively at –70 mV (vs. RHE), much larger than that of commercial 20 wt% Pt/C (530 A  $g_{Pt}^{-1}$ ) (Supplementary Fig. 32). Considering that potentiostatic electrochemical impedance spectroscopy (EIS) may be not scientifically accurate as the charge transfer is inversely proportional to the current density, we conducted EIS at a fixed current density of 1 A cm<sup>-2</sup>. The charge transfer resistance of RuPtnanoarray and metallic Ru-nanoarray-600 were 1.5 and 2.9 ohm cm<sup>2</sup>, respectively, remarkably smaller than that of the Ru NPs-nanoarray (12.3 ohm cm<sup>2</sup>) (Supplementary Fig. 33).

In OER, the overpotential for  $RuO_x$ -nanoarrays-400 was 330 mV at 1 A cm<sup>-2</sup> (Fig. 5C, D), much lower than  $RuO_x$ -nanoarrays-500 (472 mV)

and RuO<sub>x</sub>-nanoarrays-600 (532 mV). The RuO<sub>x</sub>-nanoarray-400 demonstrates a notable mass activity of 4295 A g<sub>Ru</sub><sup>-1</sup> at 1.55 V (*vs.* RHE), representing 123 folds enhancement over the commercial RuO<sub>2</sub> catalyst (35 A g<sub>Ru</sub><sup>-1</sup>) (Supplementary Fig. 34). The enhanced activity may arise from the better intrinsic activity of the relatively amorphous structures, which probably possessed more abundant defects and oxygen vacancies<sup>36</sup> (Supplementary Fig. 29). The RuO<sub>x</sub> NPs-nanoarrays showed dramatic fluctuations when the current density reached 200 mA cm<sup>-2</sup>, possibly due to the shedding of RuO<sub>x</sub> NPs. Compared to the previously reported catalysts in acidic media, the HER and OER performance of the above nanoarray catalysts was undoubtedly comparable at a high current density level (Supplementary Fig. 35, Supplementary Tables 2 and 3).

In stability tests, both the metallic Ru-nanoarray-600 and RuO<sub>x</sub>nanoarrays-400 presented negligible increase in overpotential after running the reaction at 1 A cm<sup>-2</sup> for 200 h (Fig. 5E red line, Supplementary Fig. 36), and the nanoarray architecture and crystalline structure were integrally retained (Fig. 5F right, Supplementary Figs. 37 and 38). At the same current density, the Ru NPs-nanoarray displayed an apparent increase in overpotential after 50 h (Fig. 5E green line), and a large number of Ru NPs-nanoarrays were detached from the carbon cloth fibers under the constant impact of generated



curves with *iR* correction of alloy RuPt-nanoarray, metallic Ru-nanoarray-T, Ru NPsnanoarray, Ru NPs-aggregate, commercial Pt/C decorated carbon cloth and pristine carbon cloth in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. **B** Tafel plots obtained from the polarization curves in (**A**). **C** Polarization curves with *iR* correction of RuO<sub>x</sub>-nanoarray-T,

commercial RuO<sub>2</sub> and pristine Ti fiber felt in 0.5 M  $H_2SO_4$  solution. **D** Tafel plots obtained from the polarization curves in (**C**). **E** Long-term stability measurement of the metallic Ru-nanoarray-600 and Ru NPs-nanoarray at 1 A cm<sup>-2</sup>. **F** SEM images of Ru NPs-nanoarray (left) and Ru-nanoarray-600 (right) after the chronopotentiometry testing at 1 A cm<sup>-2</sup>.

bubbles (Fig. 5F left, Supplementary Fig. 39). We also tracked the mass change of the Ru NPs-nanoarray during the test and found that the mass was decreasing as the test went on. After 50 hours of testing, the catalyst was reduced by 45%. (Supplementary Fig. 40). Thus, the extraordinary durability in acid medium of the metallic Ru-nanoarray-600 probably originated from the continuous crystalline structure and the fully metallic nanoarray. Contact angle analyses further demonstrated that the surface of metallic Ru-nanoarray-600 was hydrophilic toward the electrolyte but superaerophobic against the H<sub>2</sub> bubble (Supplementary Fig. 41), which further favored the release of the generated gas at a high current density<sup>37</sup>.

Considering the higher price of Pt, we investigated the practical application potential of cheaper Ru as catalyst in water electrolysis. A proton exchange membrane (PEM) water electrolyzer was constructed by using RuO<sub>x</sub>-nanoarrays-400 as the anode and the metallic Runanoarray-600 as the cathode (Fig. 6A, B). *I–V* curves clearly showed that RuO<sub>x</sub>-nanoarrays-400/Nafion 117/Ru-nanoarray-600 electrolyzer required only 1.88 V to reach a current density of  $2 \text{ A cm}^{-2}$  at  $80 \,^{\circ}\text{C}$  (without iR-corrected), which was considerably better than the commercial IrO<sub>2</sub>/Nafion 117/Pt/C electrolyzer and other reported systems

(Fig. 6C, Supplementary Table. 4). The voltage of the RuO<sub>x</sub>-nanoarrays-400/Nafion 117/Ru-nanoarray-600 electrolyzer showed negligible increase (degradation rate: 20 µV h<sup>-1</sup>) and the nanoarray architectures remained undamaged after operating at 1 A cm<sup>-2</sup> for more than 500 h (Fig. 6D, Supplementary Fig. 42), indicating an outstanding durability against the high current density, acidic media and bubbles impact. In contrast, the commercial RuO<sub>2</sub>/Nafion 117/Pt/C electrolyzer decay rapidly within 20 h. We monitored Ru dissolution from RuOx-nanoarrays-400/Nafion 117/Ru-nanoarray-600 electrolyzer by inductively coupled plasma mass spectrometry (ICP-MS) during 500 h stability test (Supplementary Fig. 43). The Ru concentration exhibited an initial surge during the early operational phase, reflecting dissolution of unstable Ru species during the activation period. Dissolution rates stabilized progressively during the first 200 h interval, ultimately maintaining a relatively constant level of approximately 55 ppb throughout the subsequent stability assessment phase.

#### Theoretical calculations

Density functional theory (DFT) calculations were applied to analyze the adsorption energy of \*H intermediates on the catalyst surface.



the PEM water electrolyzer using  $\rm RuO_x\text{-}nanoarrays\text{-}400$  as the anode and the metallic Ru-nanoarray-600 as the cathode and the corresponding low-

magnification SEM images. **B** The photograph of the PEM water electrolyzer device. **C** Polarization curves of PEM water electrolyzers in pure water at 80 °C. **D** Chronopotentiometry testing of PEM water electrolyzers at 1 A cm<sup>-2</sup>.

The Sabatier principle states that a catalyst should bind an H atom neither too weakly nor too strongly to achieve a better HER performance<sup>38</sup>. First of all, we constructed a model of perfect Ru (100) plane and calculated the Gibbs free energy ( $\Delta G_{\rm H}$ ) of six different adsorption sites, including the top sites  $(t_1, t_2)$ , hollow sites (h<sub>1</sub>, h<sub>2</sub>) and bridge sites (b<sub>1</sub>, b<sub>2</sub>) (Supplementary Fig. 44A). The dominant adsorption sites on perfect Ru (100) are the bridge and hollow sites (b1 & h2), which reveal highest binding energy to \*H, leading to a poor theoretical HER activity (Supplementary Fig. 44B). The NPs fusion-induced GBs in the metallic Ru-nanoarrays produced abundant atomic vacancies on the surface, whereby we constructed a defective Ru crystal by removing some atoms on the surface (Supplementary Fig. 44C). This created new catalytic sites in the vacancies  $(v_1, v_2)$ . Compared to the perfect Ru, the  $\Delta G_H$  of  $v_2$  and  $b_1$  is significantly reduced to -0.04 and -0.31 eV (Supplementary Fig. 44D), respectively, suggesting an enhanced intrinsic activity. Projected density of states (PDOS) demonstrated that the atomic vacancies in the metallic Ru-nanoarray would increase the density of states of the Ru sites near the Fermi level (Supplementary Fig. 44E). The calculated charge density of defective Ru showed distinct charge delocalization around the GBs, and the weakening of charge density at the vacancies reduces the \*H adsorption strength (Supplementary Fig. 44F). It appears that more free electrons could transfer from the catalyst to the reactant molecules with lower energy barriers driven by the electric potential, facilitating the recombination of adsorbed \*H into H<sub>2</sub>.

In summary, we have revealed an intriguing spontaneous agglomeration process of a variety of metal (Ru, Ir, Rh, Pt) NPs into erect nanoarrays with precisely controlled height and components on various substrates. By in situ smelting, one or more metal NPs fused together and recrystallized into continuous metallic, alloy or oxide nanoarray, which prominently promoted the electrolysis of water in PEM cells at industrial-level current density especially in terms of stability, as a result of the highly open space, improved electron conductivity and fully metallic nanoarrays. In principle, this approach is applicable for a wider variety of nanoparticles such as transition metals, quantum dots, clusters and perovskites. The introduction of more types of metal NPs and the cooperative smelting also provides a feasible route to the construction of high-entropy alloys with predefined nanostructures. Future work could explore synergistic integration with membrane impregnation techniques to optimize interfacial contact and mitigate mass transport limitations. The advances in the fabrication of these distinctive nanoarray materials on desired substrates are anticipated to promote upgrade applications in catalysis, thermoelectricity, solar cells, superconductivity, flexible sensors, bioelectrodes, etc.

## Methods

#### **General information**

Ethylene glycol ( $\geq$ 99.5%, AR), isopropanol (99.8%, HPLC), tetrahydrofuran (99.8%, free of stabilizer, HPLC), K<sub>2</sub>PtCl<sub>6</sub> (99.95%, RG) were purchased from Adamas. Ethanol ( $\geq$ 99.5%, GR) and sodium acetate

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( $\geq$ 99.0%, AR) were purchased from Greagent. RuCl<sub>3</sub> (97%) and IrCl<sub>3</sub> (99.9%) were purchased from Bidepharm. RhCl<sub>3</sub> (99%) was purchased from Meryer. PFS<sub>29</sub>-*b*-P2VP<sub>230</sub> block copolymer was synthesized via living anionic ROP according to previous reports<sup>39</sup>. The carbon clothes were purchased from Toray.

#### Preparation of PFS<sub>29</sub>-b-P2VP<sub>230</sub> micelle seeds

In a typical process, 5 mg of  $PFS_{29}$ -*b*-P2VP<sub>230</sub> polymer powder was added to 10 mL of isopropanol and stirred at 80 °C until the mixture became transparent. The resulting solution was aged at room temperature overnight to allow the formation of long polydisperse cylindrical micelles. Micelles were subsequently fragmentized into shorter and uniform seeds by sonication using a probe ultrasonic processor in an ice-water bath for 80 min.

#### Preparation of long PFS<sub>29</sub>-b-P2VP<sub>230</sub> cylindrical micelles

Typically, 50  $\mu$ L of a solution of unimers (10 mg mL<sup>-1</sup> in tetrahydrofuran) was added to 1 mL of the solution of micelle seeds (0.05 mg mL<sup>-1</sup> in isopropanol) to trigger the living growth at the termini of the micelle seeds. The solution was shaken for 30 min and aged for 2 h, followed by solvent exchange to ethylene glycol by evaporation.

# Living growth of $PFS_{29}$ ·*b*·P2VP<sub>230</sub> micellar brushes on desired substrates

A piece of carbon cloth (1 cm × 1 cm) was selected, and firstly sonicated alternatively in acetone and water to remove the surface-adsorbed components. Afterwards, it was treated by plasma to activate the surface and then soaked in a solution of the PFS<sub>29</sub>-*b*-P2VP<sub>230</sub> micelle seeds (500  $\mu$ L, 0.5 mg mL<sup>-1</sup> in isopropanol). After 30 min, the carbon cloth was taken out and blow dried under a gentle stream of nitrogen. The resulting carbon cloth was rinsed with isopropanol to remove the excess and poorly immobilized micelle seeds. Then, the micelle seed-coated carbon cloth was placed in 1 mL of isopropanol, followed by adding 4, 8, 16 and 32  $\mu$ L of a solution of the PFS<sub>29</sub>-*b*-P2VP<sub>230</sub> unimers (10 mg mL<sup>-1</sup> in tetrahydrofuran) and the mixture was vibrated for 30 min using a shaker. Subsequently, the resulting carbon cloth was rinsed with isopropanol cloth was rinsed with isopropanol cloth was rinsed with isopropanol cloth was rinsed in environment.

When using flat titanium (Ti) sheets or quartz glass slides as the substrate,  $20 \,\mu\text{L}$  of a solution of the micelle seeds (0.5 mg/mL in isopropanol) was cast on the substrate using a spin coater (3000 rpm, 1 min). The subsequent living growth process was the same as described above.

# Fabrication of monodisperse metal (Ru, Ir, Rh, Pt) nanoparticles with controlled sizes

Metal nanoparticles (NPs) with a narrow size distribution were synthesized by chemical reduction of their corresponding metal species in ethylene glycol<sup>40</sup>. For small metal NPs, a certain amount of the metal compound  $(3.2 \times 10^{-3} \text{ mol L}^{-1})$  and varied amount of sodium acetate  $(0.01-0.12 \text{ mol L}^{-1})$  were dissolved in 50 mL of ethylene glycol at room temperature (60 °C for RhCl<sub>3</sub> and IrCl<sub>3</sub>) under magnetic stirring. After bubbling with nitrogen for 30 min, the solutions were heated at 160 °C for 90 min. The resulting metal NPs were approximately 1.2 nm in diameter.

Metal NPs with larger sizes were further fabricated by seedmediated growth. For instance, Ru NPs with diameter of 2.1 nm were synthesized using Ru NPs (1.2 nm) as the seeds. Typically, 20 mL of a solution of the as-prepared Ru NPs (1.2 nm) was mixed with 30 mL of ethylene glycol. Subsequently, RuCl<sub>3</sub> (final concentration  $3.2 \times 10^{-3}$  mol L<sup>-1</sup>) and sodium acetate (final concentration 0.01-0.12 mol L<sup>-1</sup>) were added at room temperature (60 °C for RhCl<sub>3</sub> and IrCl<sub>3</sub>) under magnetic stirring. After bubbling with nitrogen for 30 min, the solutions were heated at 160 °C for 90 min. Similarly, Ru NPs with diameter of 3.3 nm were synthesized using Ru NPs (2.1 nm) as the seeds.

#### Preparation of nanowires of stacked metal NPs in solution

Nanowires of stacked metal NPs were prepared by mixing 2 mL of a solution of corresponding metal NPs ( $0.1 \text{ mg mL}^{-1}$  in ethylene glycol) and 1 mL of a solution of PFS<sub>29</sub>-*b*-P2VP<sub>230</sub> cylindrical micelles (0.05 mg mL<sup>-1</sup> in ethylene glycol). The mixture was shaken for 10 s and allowed to age at room temperature for 2 h.

For the preparation of nanowires of multiple simultaneously stacked metal NPs, the corresponding metal NPs in ethylene glycol were firstly mixed in a 1:1 mass ratio to obtain a hybrid solution (total concentration 0.1 mg mL<sup>-1</sup>). Subsequently, 2 mL of the hybrid solution was mixed with 1 mL of a solution of  $PFS_{29}$ -*b*-P2VP<sub>230</sub> cylindrical micelle (0.05 mg mL<sup>-1</sup> in ethylene glycol). The mixture was shaken for 10 s and allowed to age at room temperature for 2 h.

# Preparation of nanowires of sequentially agglomerated Ru and Pt NPs in solution

Typically, 1 mL of a solution of Ru NPs (3.3 nm, 0.1 mg mL<sup>-1</sup> in ethylene glycol) was firstly mixed with 1 mL of a solution of  $PFS_{29}$ -*b*-P2VP<sub>230</sub> cylindrical micelles (0.05 mg mL<sup>-1</sup> in ethylene glycol). After 10 min, 1 mL of a solution of Pt NPs (3.4 nm, 0.1 mg mL<sup>-1</sup> in ethylene glycol) was added, and the mixture was shaken for 10 s and allowed to age at room temperature for 2 h.

#### Preparation of nanoarrays of stacked metal NPs (M NPsnanoarrays)

Typically, a piece of micellar brush-decorated carbon cloth was immersed in 2 mL of a solution of metal NPs for 20 min, followed by rinsing with ethylene glycol to remove the excess metal NPs. This operation was repeated up to 5 times. Subsequently, the resulting carbon cloth was rinsed with ethanol to remove the remaining ethylene glycol. Supercritical carbon dioxide drying was applied to eliminate the capillary effect caused by the surface tension, leading to the formation of erect M NPs-nanoarrays in the dry state.

#### **Preparation of continuous metallic, alloy and oxide nanoarrays** In a typical process, individual or hybrid metal NPs-nanoarrays were heated at a high temperature (T = 400,500,600 °C) with a speed of

heated at a high temperature (T = 400, 500, 600 °C) with a speed of 10 °C min<sup>-1</sup> in specified gas atmosphere (N<sub>2</sub> for metallic and alloy nanoarrays, air or N<sub>2</sub>/O<sub>2</sub> for oxide nanoarrays) and allowed to age for 4 h before cooling to room temperature.

#### Characterizations

**Scanning electron microscopy (SEM).** SEM images were obtained on a RISE-MAGNA microscope operating at 5 keV under a high-resolution mode with a work distance of 5 mm. Energy dispersive spectrometric (EDS) mapping was performed using an Oxford X-Max Extreme operating at 15 keV under analysis mode with a work distance of 8 mm.

**Transmission electron microscopy (TEM).** TEM imaging was performed using two configurations: (1) a Talos L12OC G2 system equipped with a high-sensitivity CCD detector (120 kV), and (2) a Talos F200X G2 instrument with STEM capabilities (200 kV). For nanoparticle dispersions, samples were deposited onto carbon-coated copper grids via drop-casting followed by ambient drying. Bulk materials were subjected to brief ethanol ultrasonication (5–10 s) prior to grid deposition. Image processing utilized Velox 3.6 and FIJI/ImageJ platforms.

In situ heating experiments employed a JEM-F200 TEM (200 kV Schottky emitter) with a MEMS-based heating holder (Protochips Fusion Select). Specimens were dispersed in ethanol, loaded onto holey carbon MEMS chips (18 nm thick), and dried under infrared illumination<sup>41</sup>. Temperature ramping proceeded at 10°C min<sup>-1</sup> during time-resolved imaging.

**Contact angle**. Contact angles were measured by a Lauda Scientific LSA100 system equipped with a high-speed camera at room temperature. Two microliters of electrolyte or bubble was introduced via the sessile drop method and the angle was measured by the circle fitting approach. For each sample, at least three locations were tested in order to minimize the errors.

X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out using Thermo Scientific K-Alpha. The obtained data were analyzed by Avantage software.

**X-ray diffraction (XRD).** XRD patterns were obtained on Rigaku Smartlab 9KW with a grazing incidence of 0.3°. Samples for XRD measurements were placed on quartz glass slides.

**Inductively coupled plasma-mass spectrometry (ICP-MS)**. ICP-MS data were collected using the NexION2000 Flexar20 HPLC system.

**Electron conduction measurements.** Electron conductivity analyses were performed at ambient conditions using a Bruker Dimension FastScan Bio atomic force microscopy with an electrical & magnetic module and a Multi75E-G probe, utilizing peak force tuna feedback control. Samples of metal nanoarrays were fabricated on a conductive titanium sheet before the test. The titanium sheet and the test platform were bonded together using conductive copper glue. The electron conductivity  $\sigma$  can be calculated as

$$\sigma = \frac{\nabla I}{\nabla V} \times \frac{H}{A} \tag{1}$$

where  $\nabla I$  and  $\nabla V$  were the current and bias voltage calculated from the *I*-*V* curves, *H* and *A* represented the height and cross-section area of the nanowire, respectively.

Electrocatalytic measurements. Electrocatalytic performance was assessed using a three-electrode electrochemical cell (CH Instrument 760E). The as-prepared samples of the Ru NPs-aggregate on carbon cloth, metal NPs-nanoarrays and metallic nanoarray on carbon cloth  $(1 \text{ cm} \times 1 \text{ cm}, \text{ containing } ca. 0.22 \text{ mg of catalyst})$  were directly used as the working electrodes. The 20 wt% Pt/C electrodes were fabricated by depositing 100  $\mu$ L of catalysts ink (5.5 mg catalysts + 20  $\mu$ L of Nafion solution in 2.5 mL of a mixture of 1:1 (v/v) water and isopropanol) onto carbon cloth, followed by drying at 60 °C. The test area for all samples is 1 cm<sup>2</sup>, unless otherwise noted. A saturated calomel electrode (SCE) and a platinum flake were used as the reference and counter electrodes, respectively. An aqueous solution of  $H_2SO_4$  (0.5 M, pH =  $0.01 \pm 0.01$ ) was used as the electrolyte, which was configured by dilution with sulfuric acid and stored at room temperature in a sealed glass bottle. Before testing, the SCE was calibrated following established protocols<sup>42</sup>. Typically, Pt flake was selected as both the working electrode and counter electrode. The electrolyte (0.5 M H<sub>2</sub>SO<sub>4</sub>) was saturated with H<sub>2</sub> for at least 30 min. CV was carried out at a scan rate of 1 mV s<sup>-1</sup>, and the average of the two interconversion point values was taken as the thermodynamic potential. The experimentally value of  $E^{0}$ (SCE) is 0.243 V in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The deviation was <5 mV compared to the theoretically value (0.241 V). All the mentioned potential was referenced to the reversible hydrogen electrode (RHE) according to the following equation:  $E(RHE) = E(vs. SCE) + E^{0}(SCE) + 0.059 \text{ pH}$ . Linear sweep voltammetry (LSV) measurements were conducted at 5 mV s<sup>-1</sup> and results were corrected by *iR* compensation ( $E_{iR-corrected} =$  $E_{\text{original}} - I \times 0.85R$ s). Tests were performed three times to minimize accidents and errors. The stability was tested at a current density of 1 A cm<sup>-2</sup> with *iR* correction for 200 h by chronopotentiometry. Electrochemical impedance spectra (EIS) were acquired at 1 A cm<sup>-2</sup> in a frequency range of 100,000–0.01 Hz. The electrochemically active surface area (ECSA) was determined by: ECSA =  $C_{\rm dl}/C_{\rm s}$ , ( $C_{\rm dl}$ : double-layer capacitance,  $C_{\rm s}$ : specific capacitance)<sup>43</sup>. In this study, a general specific capacitance of  $C_{\rm s} = 0.035$  mF cm<sup>-2</sup> was used based on the typical reported values<sup>44</sup>.  $C_{\rm dl}$  was determined by the equation  $C_{\rm dl} = i_c/v$ , ( $i_c$ : charging current, v: scan rate). A plot of  $i_c$  as a function of v yields a straight line with a slope equal to  $C_{\rm dl}$ .

PEM water electrolyzer tests. A self-made cell was used as the PEM water electrolyzer device. The PEM cell consists of an iridium-coated titanium plate at the anode and a titanium plate at the cathode with serpentine flow channels of 1.6 cm<sup>2</sup> area on both sides. The Nafion 117 membranes were boiled sequentially for 1 h each in 3 wt.% H<sub>2</sub>O<sub>2</sub>, pure water, 1.0 M H<sub>2</sub>SO<sub>4</sub> and pure water to remove possible contaminants and ensure the membrane was completely protonated. The RuO<sub>x</sub>nanoarray-400 on a titanium fiber felt, and the metallic Ru-nanoarray-600 on a carbon cloth were used as an OER anode and a HER cathode, respectively. Both of them were coated with 10 wt.% Nafion ionomers before being assembled into the membrane electrode assembly, followed by hot-pressing on a Nafion membranes at 135 °C at a mold clamping force of 2 MPa for 3 min<sup>45</sup>. The electrolyzer underwent exposure to water at 80 °C for no less than 5 h. Prior to testing, the electrolyzer underwent sequential testing for galvanostatic (at 0.1 A cm<sup>-2</sup>) and potentiostatic (at 1.6 V) for 0.5 h each step to achieve a steady-state. The cell was then circulated with pure water at 100 mL min<sup>-1</sup>. *I–V* curves were measured at 80 °C.

Molecular dynamics calculation. In order to explore the interaction between PFS<sub>29</sub>-b-P2VP<sub>230</sub> cylindrical micelles and Ru NPs, two simplified all-atom models were constructed. First, for computational convenience, a nanotube structure was used to represent the PFS core, in consideration of the factor that the Ru NPs predominantly interact with the P2VP corona chains. On this basis, the P2VP chains were grafted onto the surface of the nanotubes with an equal spacing of 3.5 nm. At the same time, for the convenience of calculation, the repeating unit of P2VP is set as 20. In addition, three types of Ru NPs with variable diameters were constructed to investigate the effect of nanoparticle size. Universal force field was used to describe the cylindrical micelles and Ru NPs. At the beginning of the simulation, six NPs were placed in the gaps of the P2VP chains. Then, smart algorithm was used to minimize the energy of the system. At last, 1 ns constant volume-temperature run was performed at 298 K to obtain the equilibrium structure. Nose-Hoover thermostat was employed to control the temperature.

**Theoretical methods for HER.** All density functional theory (DFT) calculations in this study are performed using Vienna ab initio simulation package (VASP) code<sup>46,47</sup>. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional is used to describe the exchange-correlation energy<sup>48</sup>. The project augmented wave (PAW) method<sup>49</sup> is employed and the cutoff energy was set to 450 eV. The convergence limitation for force and energy are set as 0.05 eV Å<sup>-1</sup> and 10<sup>-4</sup> eV, respectively. The Brillouin zones are sampled by Monkhorst–Pack scheme<sup>50</sup>, which is carried out automatically by using VASPKIT package<sup>51</sup>. The k-points separation length is set as 0.04  $2\pi$  Å<sup>-1</sup> for geometric optimization. A finer separation length, 0.02  $2\pi$  Å<sup>-1</sup> is used in density of state (DOS) calculations. For all surface calculations, the long-range dispersion energy interaction is corrected using the Grimme's DFT-D3 method<sup>52,53</sup>. The dipolar correction is considered and the symmetrization is switched off.

For the *hcp* Ru (1000) model, a  $(4 \times 4)$  supercell was constructed by cleaving the bulk structure along the (1000) direction, including 4 metallic atom layers. Then, two sets of Ru atoms located in the first layer are removed out from the Ru (1000) model to simulate the vacancies observed in the TEM image. A 15 Å vacuum layer was added to the slab models to prevent the periodic interactions. During the whole surface calculation process, the bottom two layers were kept frozen, while the upper two layers were fully relaxed.

The Gibbs free-energy of adsorbed H on the surface ( $\Delta G_{H^*}$ ) was evaluated by using the following equation<sup>54</sup>:

$$\Delta G_{H^*} = E_{H^*} - E^* - 1/2E_{H_2} + (\Delta ZPE - T\Delta S)$$
(2)

in which  $E_{H^{i}}$ ,  $E^{*}$  and  $E_{H_{2}}$  were the DFT energies for the adsorbed surface, the initial surface and a single H<sub>2</sub> molecule, respectively. The  $\Delta ZPE$  was the zero-point energy change  $(\Delta ZPE = ZPE_{H^{i}} - 1/2ZPE_{H_{2}})$ . The  $T\Delta S$  was entropy change  $(T\Delta S = TS_{H^{i}} - 1/2TS_{H_{2}})$ . Considering the negligible vibrational entropy for the adsorbed H\*  $(TS_{H^{i}} = 0)$ , thus, at the condition of 1 atm and 300 K,  $T\Delta S = -1/2TS_{H_{2}} = -0.205eV$ .

#### Computation of d-band center

The *d*-band center ( $\varepsilon_d$ ) was calculated from the following equation<sup>55</sup>

$$\varepsilon_d = \frac{\int_{-\infty}^{\infty} n_d(\varepsilon) \varepsilon d\varepsilon}{\int_{-\infty}^{\infty} n_d(\varepsilon) d\varepsilon}$$
(3)

where  $\varepsilon$  was energy referring to  $E_{\text{Fermi level}}$ ,  $n_d(\varepsilon)$  was the density of states data plotted versus energy.

#### Data availability

All data supporting the findings of this study are available within the article and its Supplementary Information/Source Date file, or from the authors upon reasonable request. The atomic structures for DFT calculations can be found at https://doi.org/10.6084/m9.figshare. 29117933.v1. Source data are provided with this paper.

#### References

- Turner, J. A. Sustainable hydrogen production. Science 305, 972–974 (2004).
- 2. Chu, S. & Majumdar, A. Opportunities and challenges for a sustainable energy future. *Nature* **488**, 294–303 (2012).
- Seh, Z. W. et al. Combining theory and experiment in electrocatalysis: insights into materials design. *Science* **355**, eaad4998 (2017).
- 4. Klose, C. et al. All-hydrocarbon MEA for PEM water electrolysis combining low hydrogen crossover and high efficiency. *Adv. Energy Mater.* **10**, 1903995 (2020).
- Wang, Y. et al. PEM Fuel cell and electrolysis cell technologies and hydrogen infrastructure development–a review. *Energy Environ. Sci.* 15, 2288–2328 (2022).
- King, L. A. et al. A non-precious metal hydrogen catalyst in a commercial polymer electrolyte membrane electrolyser. *Nat. Nanotechnol.* 14, 1071–1074 (2019).
- Khan, M. A. et al. Seawater electrolysis for hydrogen production: a solution looking for a problem. *Energy Environ. Sci.* 14, 4831–4839 (2021).
- Pham, C. V. et al. Essentials of high performance water electrolyzers-from catalyst layer materials to electrode engineering. Adv. Energy Mater. 11, 2101998 (2021).
- 9. Kong, S. et al. Acid-stable manganese oxides for proton exchange membrane water electrolysis. *Nat. Catal.* **7**, 1–10 (2024).
- Lagadec, M. F. & Grimaud, A. Water electrolysers with closed and open electrochemical systems. *Nat Mater.* 19, 1140–1150 (2020).
- Hao, S. et al. Torsion strained iridium oxide for efficient acidic water oxidation in proton exchange membrane electrolyzers. *Nat. Nanotechnol.* 16, 1371–1377 (2021).
- 12. Shi, Z. et al. Phase-dependent growth of Pt on  $MoS_2$  for highly efficient H<sub>2</sub> evolution. *Nature* **621**, 300–305 (2023).

- Wu, Z. Y. et al. Non-iridium-based electrocatalyst for durable acidic oxygen evolution reaction in proton exchange membrane water electrolysis. *Nat. Mater.* 22, 100–108 (2023).
- Luo, Y., Zhang, Z., Chhowalla, M. & Liu, B. Recent advances in design of electrocatalysts for high-current-density water splitting. *Adv. Mater.* 34, 2108133 (2022).
- Hou, J. et al. Rational design of nanoarray architectures for electrocatalytic water splitting. Adv. Funct. Mater. 29, 1808367 (2019).
- Tang, C. et al. Energy-saving electrolytic hydrogen generation: Ni<sub>2</sub>P nanoarray as a high-performance non-noble-metal Electrocatalyst. *Angew. Chem. Int. Ed.* 56, 842–846 (2017).
- He, S. et al. The Secret of Nanoarrays toward efficient electrochemical water splitting: a vision of self-dynamic electrolyte. *Adv. Mater.* 35, 2307017 (2023).
- Zhu, S., Sheng, J., Ni, J. & Li, Y. 3D vertical arrays of nanomaterials for microscaled energy storage devices. Acc. Mater. Res. 2, 1215–1226 (2021).
- Mor, G. K. et al. A review on highly ordered, vertically oriented TiO<sub>2</sub> nanotube arrays: Fabrication, material properties, and solar energy applications. Sol. Energy Mater. Sol. Cells **90**, 2011–2075 (2006).
- Elnathan, R., Kwiat, M., Patolsky, F. & Voelcker, N. H. Engineering vertically aligned semiconductor nanowire arrays for applications in the life sciences. *Nano Today* 9, 172–196 (2014).
- 21. Park, W. I. & Yi, G.-C. Electroluminescence in n-ZnO nanorod arrays vertically grown on p-GaN. *Adv. Mater.* **16**, 87–90 (2004).
- Ren, Z., Guo, Y. & Gao, P. X. Nano-array based monolithic catalysts: concept, rational materials design and tunable catalytic performance. *Catal. Today* 258, 441–453 (2015).
- Mishra, R. K. et al. Continuous opioid monitoring along with nerve agents on a wearable microneedle sensor array. J. Am. Chem. Soc. 142, 5991–5995 (2020).
- 24. Zhu, Q. B. et al. A flexible ultrasensitive optoelectronic sensor array for neuromorphic vision systems. *Nat. Commun.* **12**, 1798 (2021).
- Li, H. et. al. Systematic design of superaerophobic nanotube-array electrode comprised of transition-metal sulfides for overall water splitting. *Nat. Commun.* 9, 2452 (2018).
- Zhou, D. et. al. Layered double hydroxide-based electrocatalysts for the oxygen evolution reaction: identification and tailoring of active sites, and superaerophobic nanoarray electrode assembly. *Chem.* Soc. Rev. 50, 8790–8817 (2021).
- 27. Lv, X. et al. Atomic-level surface engineering of nickel phosphide nanoarrays for efficient electrocatalytic water splitting at large current density. *Adv. Funct. Mater.* **33**, 2205161 (2023).
- Cheng, J. et al. Impact of Ir-valence control and surface nanostructure on oxygen evolution reaction over a highly efficient Ir-TiO<sub>2</sub> nanorod catalyst. ACS Catal. 9, 6974–6986 (2019).
- 29. Zhou, L. et al. Stabilizing non-iridium active sites by nonstoichiometric oxide for acidic water oxidation at high current density. *Nat. Commun.* **14**, 7644 (2023).
- Cai, J. D. et al. Tailored multifunctional micellar brushes via crystallization-driven growth from a surface. Science 366, 1095–1098 (2019).
- Lin, G. Y. et al. Capillary-bound dense micelle brush supports for continuous flow catalysis. *Angew. Chem. Int. Ed.* 60, 24637–24643 (2021).
- Tian, J. et al. High-resolution cryo-electron microscopy structure of block copolymer nanofibres with a crystalline core. *Nat. Mater.* 22, 786–792 (2023).
- 33. Wen, Y. et al. A coherent nanomechanical oscillator driven by single-electron tunnelling. *Nat. Phys.* **16**, 75–82 (2020).
- 34. Warren, S. C. et al. Generalized route to metal nanoparticles with liquid behavior. *J. Am. Chem.* Soc. **128**, 12074–12075 (2006).
- Yu, J. et al. Ultra-high thermal stability of sputtering reconstructed Cu-based catalysts. *Nat. Commun.* 12, 7209 (2021).

- Deka, N. et al. On the operando structure of ruthenium oxides during the oxygen evolution reaction in acidic media. ACS Catal. 13, 7488–7498 (2023).
- Yu, X. X. et al. Superaerophobic" nickel phosphide nanoarray catalyst for efficient hydrogen evolution at ultrahigh current densities. *J. Am. Chem.* Soc. **141**, 7537–7543 (2019).
- Sun, F. et al. Theoretical advances in understanding and designing the active sites for hydrogen evolution reaction. ACS Catal. 12, 8404–8433 (2022).
- Wang, H. et al. Synthesis and self-assembly of poly(ferrocenyldimethylsilane-b-2-vinylpyridine) diblock copolymers. *Macromolecules* 40, 3784–3789 (2007).
- Wang, Y. et al. Preparation of tractable platinum, rhodium, and ruthenium nanoclusters with small particle size in organic media. *Chem. Mater.* 12, 1622–1627 (2000).
- 41. Ling, Y. et al. Atomic-level structural responsiveness to environmental conditions from 3D electron diffraction. *Nat. Commun* **13**, 6625 (2022).
- 42. Niu, S. et al. How to reliably report the overpotential of an electrocatalyst. ACS Energy Lett. 5, 1083–1087 (2020).
- Zhao, X. et al. Electrolyte-free electrochemical oxygen generator for providing sterile and medical-grade oxygen in household applications. *Device* 2, 100360 (2024).
- McCrory, C. C. L. et al. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. J. Am. Chem. Soc. 135, 16977–16987 (2013).
- Li, A. et al. Atomically dispersed hexavalent iridium oxide from MnO<sub>2</sub> reduction for oxygen evolution catalysis. *Science* **384**, 666–670 (2024).
- Perdew, J. P. et al. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- Kresse, G. et al. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater.* Sci. 6, 15–50 (1996).
- Kresse, G. et al. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 54, 11169–11186 (1996).
- Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* 50, 17953–17979 (1994).
- Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* 13, 5188–5192 (1976).
- 51. Wang, V. et al. VASPKIT: A user-friendly interface facilitating highthroughput computing and analysis using VASP code. *Comput. Phys. Commun.* **267**, 108033 (2021).
- Grimme, S. et al. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 132, 154104 (2010).
- Grimme, S., Ehrlich, S. & Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* 32, 1456–1465 (2011).
- 54. Nørskov, J. K. et al. Trends in the exchange current for hydrogen evolution. *J. Electrochem. Soc.* **152**, J23 (2005).
- Vojvodic, A., Nørskov, J. K. & Abild-Pedersen, F. Electronic structure effects in transition metal surface chemistry. *Top Catal.* 57, 25–32 (2014).

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## **Author contributions**

J.T. and H.Q. conceived the project; J.T. performed the synthetic and assembly experiments; J.T., R.G. and Y.S. performed the electrochemical tests; C.C. and Y.M. performed the in situ TEM tests; G.L. prepared the polymer samples; C.Y. performed the molecular dynamics simulations; J.T. and H.Q. analyzed the data and prepared the manuscript.

## **Competing interests**

The authors declare no competing interests.

## **Additional information**

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