

Electronic Supplementary Information (ESI) for

Polyoxometalate-modified platinum enables enhanced hydrogen evolution in buffered electrolytes

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Experimental Details

Instrumental and reagents: Transmission electron microscope (TEM) observations were conducted by JEM-2010F at an acceleration voltage of 200 kV, and scanning transmission electron microscopy (STEM) observations were conducted by JEM-ARM200F Thermal FE at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on ULVAC-PHI PHI5000 VersaProbeIII at the Advanced Characterisation Nanotechnology Platform of The University of Tokyo. The samples were embedded in conductive carbon tape and brought into the introduction chamber. The fitting of experimental data was conducted using a Multipak software (version 9.2.0.5, by Ulvac-phi, inc.) in which the Shirley method was used for the background and a Gauss–Lorentz type function was performed for fitting. The binding energies were calibrated by using the C 1s signal of C–C bonding at 284.6 eV based on our previous findings of POM-protected gold nanoparticles.^[S1] Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were conducted using Shimadzu ICPS-8100. Atomic absorption spectrometry (AAS) analyses were conducted by Hitachi ZA3000. Infrared (IR) spectra were measured on JASCO FT/IR-4100 using the attenuated total reflection method. Electrochemical measurement using a 16-channel research-grade potentiostat system (VMP3, BioLogic Science Instruments, Grenoble, France). All chemical reagents were obtained from Tokyo Chemical Industry, Aldrich, Kanto Chemical, or FUJIFILM Wako Pure Chemical (reagent grade) without pretreatment. Inorganic salts of **SiW12** ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$) and **Nb6** ($\text{K}_8\text{Nb}_6\text{O}_{19}$) were purchased from KANTO chemical and MITSUWA chemical respectively. Commercial catalysts Pt/Vulcan (SKU: 57080081, Vulcan XC 72) and Ru/Vulcan (SKU: 57080103, Vulcan XC 72) were purchased from FUELCELL store.

Preparation of inorganic salts of SiW9 ($\text{Na}_{10}\text{SiW}_9\text{O}_{34}$) in a slightly modified method of previous report:^[S2] $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (182 g, 0.55 mol) and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (11 g, 50 mmol) were dissolved in 200 mL of hot water (85 °C) in a 1 L beaker containing a magnetic stirring bar. To this solution was added dropwise 130 mL of 6 M HCl in ~30 min with vigorous stirring, and the solution was boiled until the volume was 300 mL while the unreacted silica was removed by filtration. Na_2CO_3 (50 g, 0.47 mol) was dissolved in 150 mL of water in a separate beaker, which was slowly added to the first solution with gentle stirring for 3 h. The white precipitates were collected by filtration, and re-dispersed in a 1 L solution containing 4 M

NaCl while stirring for 3 min, followed by filtration. It is then washed successively with two 100 mL portions of ethanol and 100 mL of diethyl ether and dried under vacuum.

Preparation of SiW9-modified metal nanoparticle catalysts (SiW9-Pt/Vulcan and SiW9-Ru/Vulcan):

SiW9 (3.0 g, 1.2 mmol POM) was dissolved in water (300 mL), to which was added 150 mg Pt/Vulcan (150 mg, 0.15 mmol Pt). After stirring the solution for 4 h min, the solution was filtrated by the membrane, washed with H₂O (75 mL x 2), and dried overnight under vacuum to give **SiW9-Pt/Vulcan**. The contents of Pt and W in **SiW9-Pt/Vulcan** are summarized in Table S1. Vulcan carbon without Pt was immersed in an aqueous solution of **SiW9** and subsequently analyzed by ICP-AES while no detectable adsorption of SiW9 onto Vulcan was observed. The surface coverage of **SiW9** on Pt was calculated based on these content values, which is discussed in the manuscript. The Na content was also determined to be 0.8 wt% (Table S1), and the experimentally observed Na : W ratio was 11.4 : 9, which is close to the theoretical ratio of 10 : 9 (Na₁₀SiW₉O₃₄). As for **SiW9-Ru/Vulcan**, the same procedures were used with the exception of using 1.5 g **SiW9**. **SiW12-Pt/Vulcan** and **Nb6-Pt/Vulcan** were prepared using similar procedures as that for **SiW9-Pt/Vulcan**, except for using different POMs (H₄SiW₁₂O₄₀, K₈Nb₆O₁₉). The filtrate was freeze-dried and taken for IR analysis. As for the test using carbon paper, commercial carbon paper with loaded Pt/Vulcan (40 wt.%, 0.3 mg_{Pt}/cm²) was immersed in the solution of **SiW9** (keeping the ratio of **SiW9** to Pt as 8 : 1) for 1 day, and then taken for electrochemical test.

Electrochemical measurements: A three-electrode system was used including the catalyst-loaded glassy carbon (GC) rotating disk electrode (RDE, S = 0.0707 cm²), the Pt wire encapsulated in and protected by proton exchange membrane, and the Ag/AgCl electrode (saturated KCl, BAS Inc.) electrode, as the working electrode, the counter electrode, and the reference electrode, respectively. Prior to each experiment, a GC RDE was thoroughly polished using a 0.05- μ m alumina (BAS Inc.), followed by 10-minute ultrasonic cleaning in ethanol. The catalyst-loaded GC RDE was cleaned electrochemically using cyclic voltammetry (CV) with cycling between approximately -0.1 V and 1.28 V versus the reversible hydrogen electrode (RHE) with hydrogen bubbling ($\geq 99.9999\%$). The homogeneous dispersed solution was obtained by sonicating 5 mg of electrocatalysts in 5 mL isopropyl alcohol, 5 mL deionized water, and 20 μ L of 20 wt.% Nafion. After sonicating for 20 min, 1.765 μ L of the homogeneous ink was dropped onto the GC RDE (ca.

2.5 $\mu\text{g}\cdot\text{cm}^{-2}$). For the carbon paper system, experiments were conducted under stationary conditions (i.e., without rotation). The electrolyte temperature was managed by immersing the electrochemical cell in a water bath or using a water-jacketed glass cell (BAS Inc.) with an external temperature control system (NCB-1210, Eyela, Tokyo, Japan). *iR* correction was performed using impedance values measured at frequencies of at least 100 kHz with an amplitude of 10 mV.

Recovery of POMs from SiW9-Pt/Vulcan after reaction by modification of a previous method:^{[S3,}

^{S4]} A homogeneous dispersion was prepared by sonicating 50 mg of electrocatalysts in 1 mL isopropyl alcohol, 1 mL of deionized water, and 125 μL of 20 wt.% Nafion. After sonicating for 60 min in an ice bath, 100 μL of the homogeneous ink was dropped onto the GC RDE with continuous drop-cast (ca. 5 $\text{mg}\cdot\text{cm}^{-2}$). Following the same setup in an aqueous buffer solution at pH 9.2 containing 0.5 mol kg^{-1} K-phosphate + 1.5 mol kg^{-1} K-borate at 70 °C under H_2 bubbling after chronopotentiometry measurements, the catalysts were scraped off from GC RDE. These procedures were repeated five times to collect a sufficient amount of solid samples, which were then dispersed in 15 mL deionized water. Subsequently, 5.0 g of ammonium chloride was added to the above dispersion, followed by stirring for 12 h to salt out the POMs, and the dispersion was filtrated. Then, 2.0 g of cesium triflate was added to the filtrate to precipitate POMs, followed by membrane filtration and wash with excessive amount of deionized water. The resulting solid was collected for IR analysis. In addition, the ICP-AES analysis of the remaining solid residue of SiW9-Pt/Vulcan after salting out with ammonium chloride revealed that the remaining W species is below the detection limit, indicating most W species were extracted by the salting out experiments.

Supplementary Figures

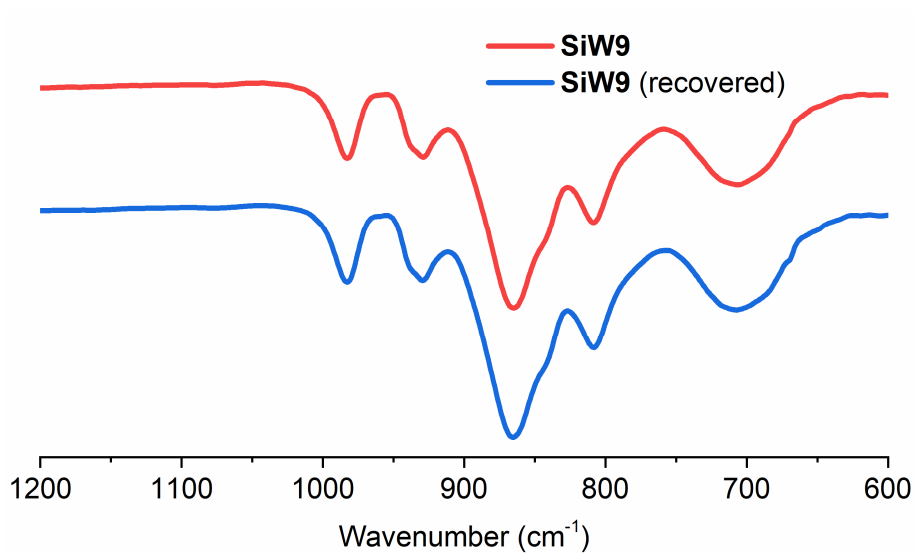


Fig. S1 IR spectra of **SiW9** and recovered **SiW9** from the filtrate of the synthetic solution.

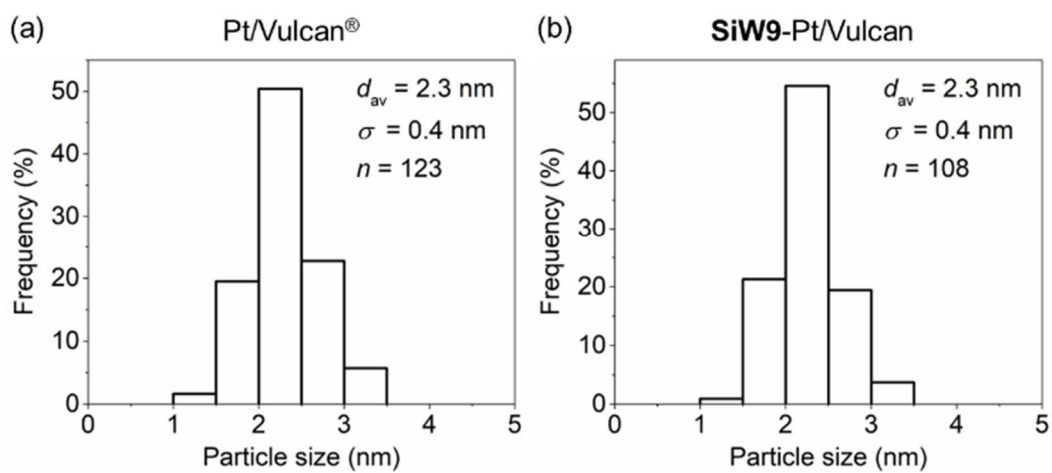
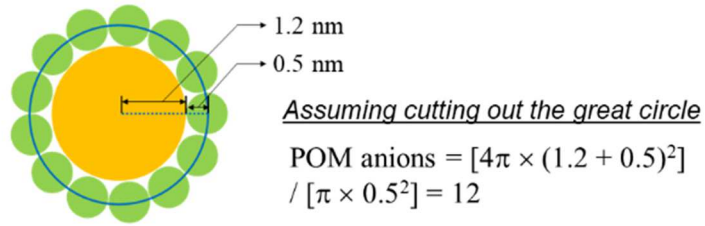


Fig. S2 Size distribution histograms of (a) Pt/Vulcan, (b) **SiW9**-Pt/Vulcan.

Maximal stacking



A possible structure for SiW9-Pt/Vulcan

According to Mackay formula,

$$\text{Pt atoms} = \frac{1}{3} \times (10 \times 4.5^3 - 15 \times 4.5^2 + 11 \times 4.5 - 3) = 218$$

$$\text{Surface POM anions per Pt particle} = 0.031 \times 218 \approx 6$$

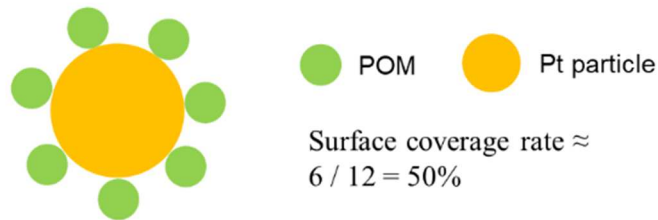


Fig. S3 Illustration for SiW9-Pt/Vulcan with estimation of surface coverage.

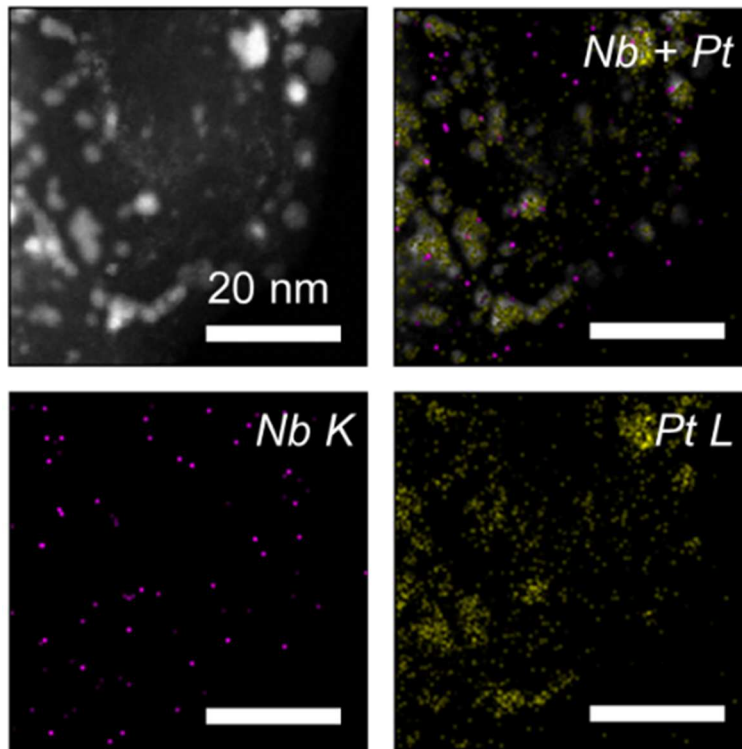


Fig. S4 STEM-EDS mapping images of Nb6-Pt/Vulcan.

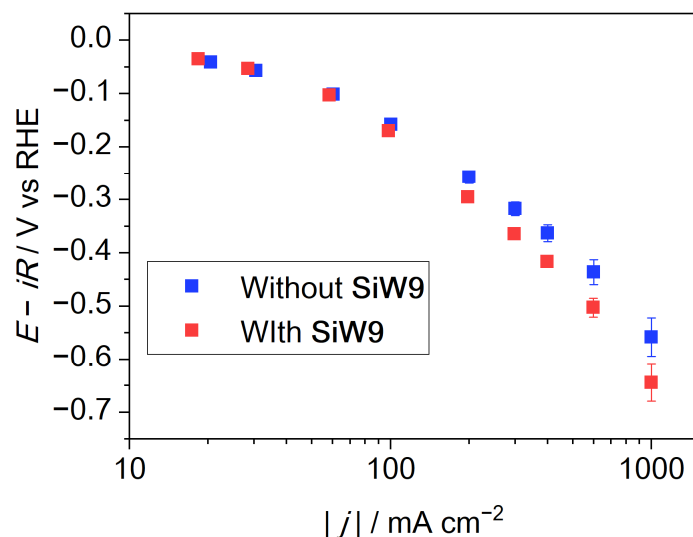


Fig. S5 Tafel plots of the Pt/Vulcan/carbon paper (blue) and the **SiW9**-Pt/Vulcan/carbon paper (red) in an aqueous buffer solution at pH 9.2 containing 0.5 mol kg^{-1} K-phosphate + 1.5 mol kg^{-1} K-borate at $80 \text{ }^\circ\text{C}$ with H_2 bubbling, based on chronopotentiometry measurements. The loading amount of Pt on the carbon paper is 0.3 mg cm^{-2} . The Pt ratio in the loaded Pt/Vulcan is 40% (w/w).

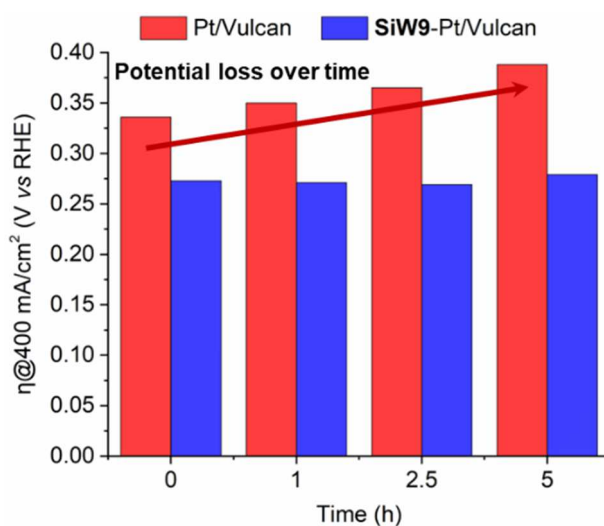


Fig. S6 Overpotentials over time regarding the durability test of Pt/Vulcan and **SiW9**-Pt/Vulcan at 400 mA/cm^2 in an aqueous buffer solution at pH 9.2 containing 0.5 mol kg^{-1} K-phosphate + 1.5 mol kg^{-1} K-borate at $80 \text{ }^\circ\text{C}$ with H_2 bubbling.

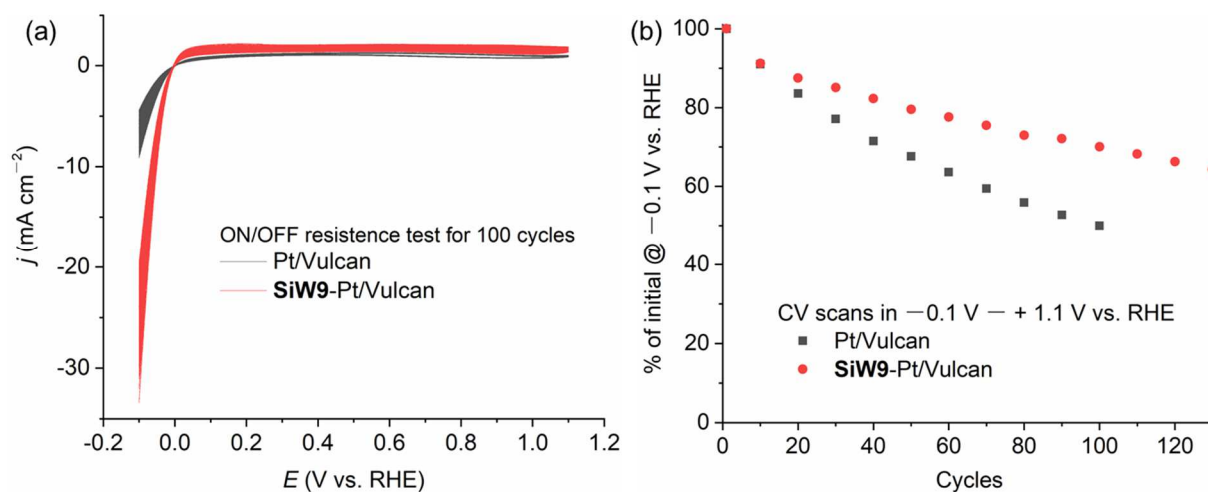


Fig. S7 ON/OFF operation test of Pt/Vulcan and **SiW9**-Pt/Vulcan in an aqueous buffer solution at pH 9.2 containing 0.5 mol kg^{-1} K-phosphate + 1.5 mol kg^{-1} K-borate at room temperature with H_2 bubbling of (a) consecutive CV scan results, and (b) cathodic current density (HER activity) at $-0.1 \text{ V}_{\text{RHE}}$ after each 10 cycles to each respective anodic edge. The loading amount of Pt on RDE is $2.5 \text{ } \mu\text{g cm}^{-2}$.

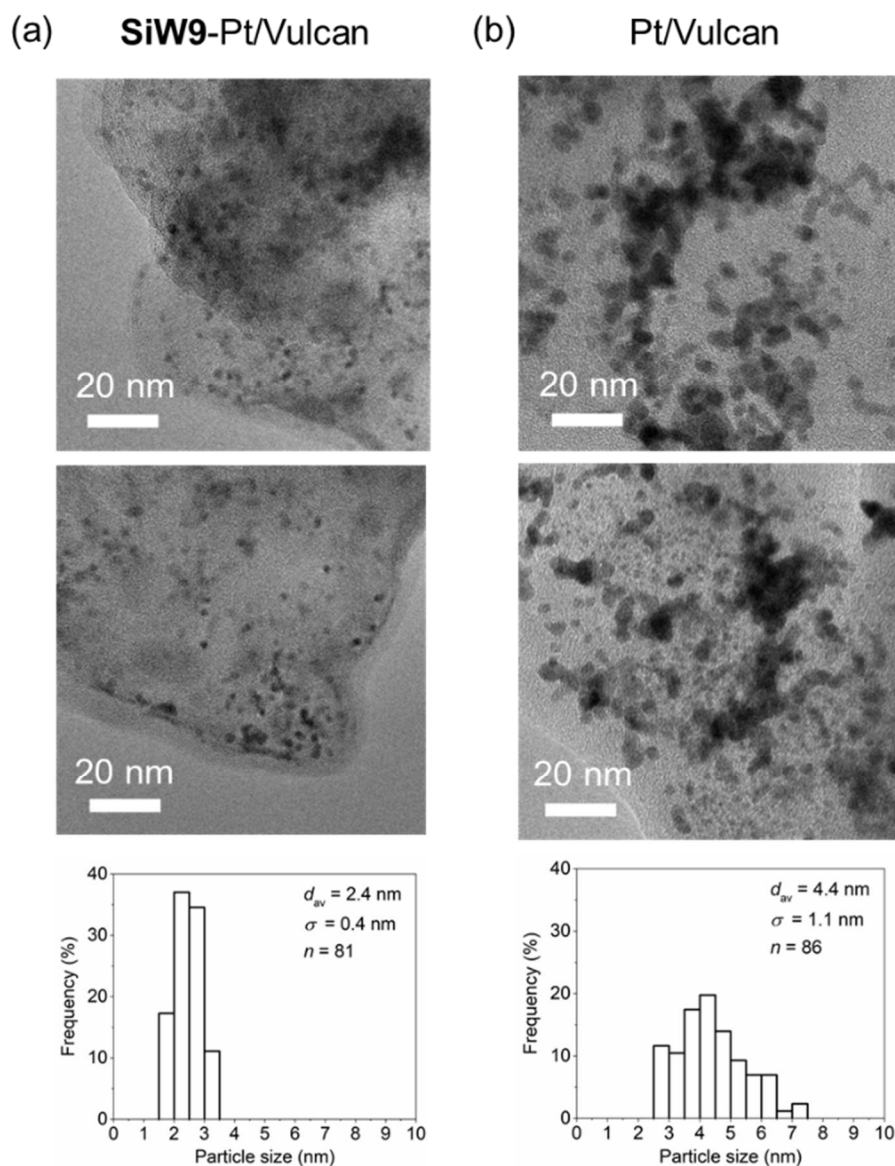


Fig S8 TEM images and corresponding histograms of size distribution of Pt nanoparticle catalysts after electrolysis for 5 hours at 400 mA cm^{-2} of (a) **SiW9-Pt/Vulcan** and (b) **Pt/Vulcan**.

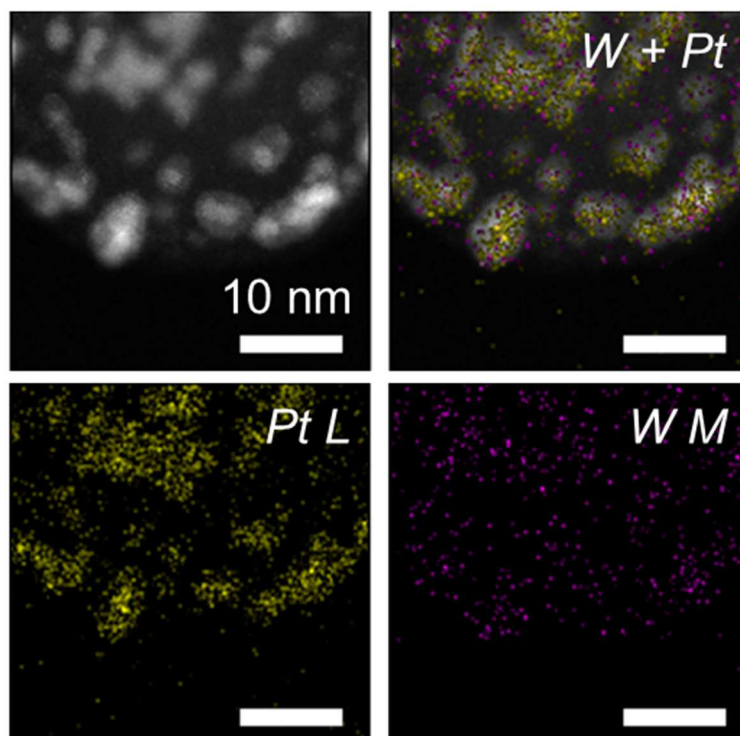


Fig. S9 STEM-EDS mapping images of **SiW9-Pt/Vulcan** catalysts after electrolysis for 5 h at 400 mA cm^{-2} (corresponding to Fig. S8a).

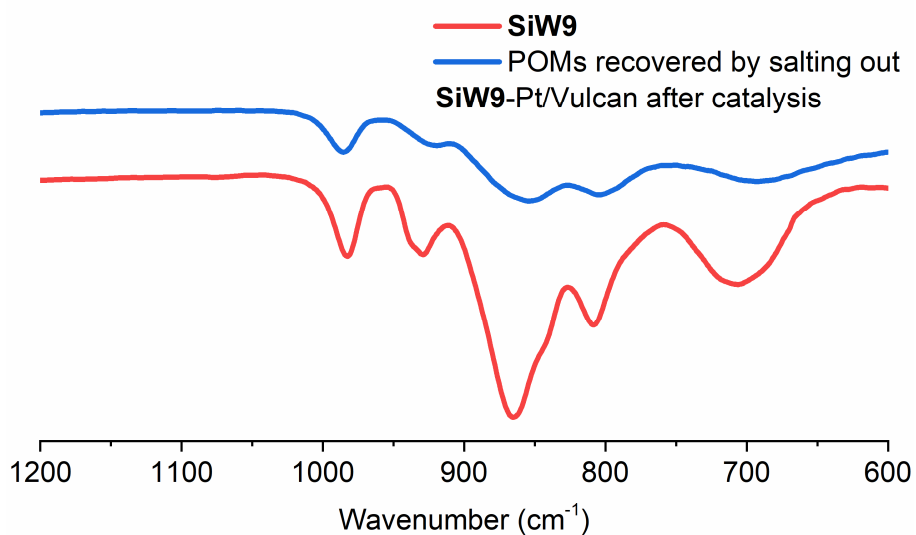


Fig. S10 IR spectra of **SiW9** and POMs recovered by salting out **SiW9-Pt/Vulcan** after the RDE test in an aqueous buffer solution at pH 9.2 of 0.5 mol kg^{-1} K-phosphate + 1.5 mol kg^{-1} K-borate at $70 \text{ }^\circ\text{C}$ with H_2 bubbling. The loading amount of Pt on RDE is 5 mg cm^{-2} .

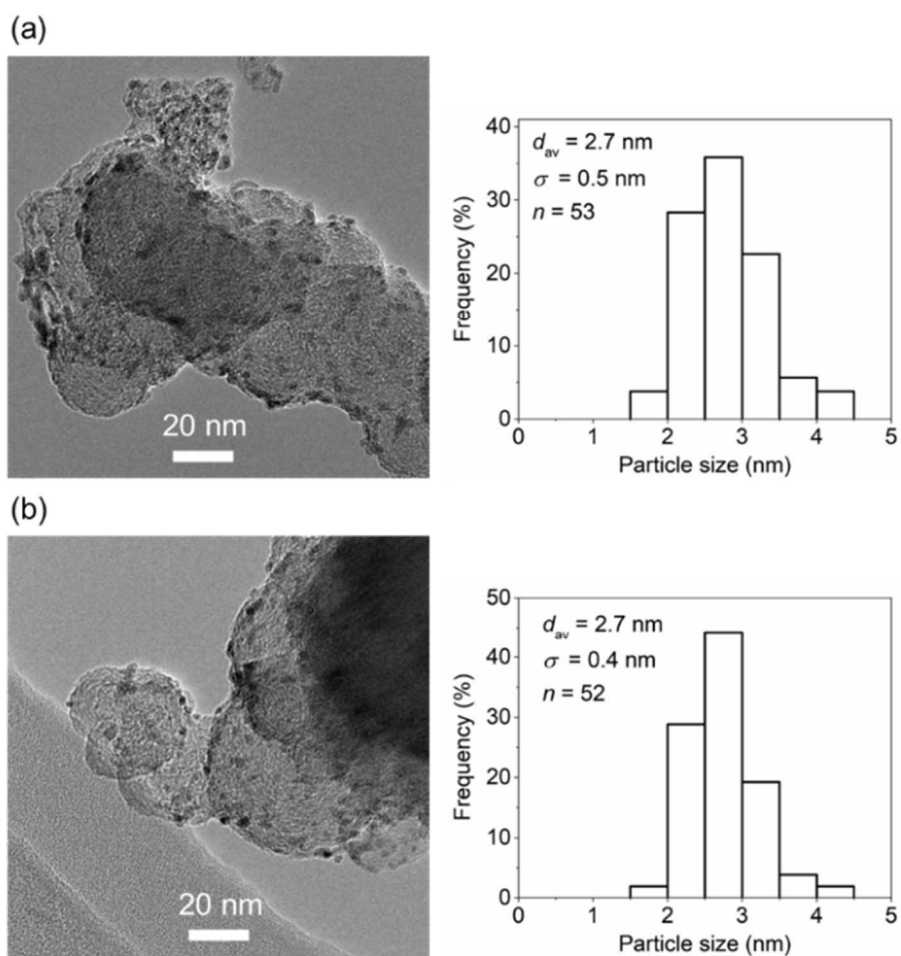


Fig. S11 TEM image and corresponding size distribution histograms of (a) Ru/Vulcan and (b) SiW9-Ru/Vulcan.

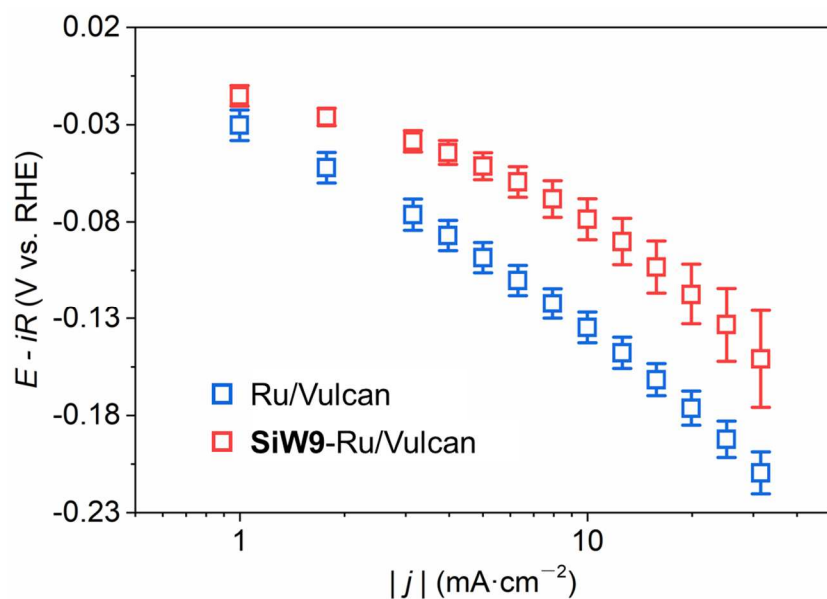


Fig. S12 $j - E$ curve and Tafel plots of the Ru/Vulcan/GC RDE electrode (blue) and the **SiW9**-Ru/Vulcan/GC electrode (red) in an aqueous buffer solution at pH 10.5 (3 M K-carbonate buffer) at 80 °C with H_2 bubbling, based on chronopotentiometry measurements. The loading amount of Ru on RDE is $2.5 \mu\text{g cm}^{-2}$.

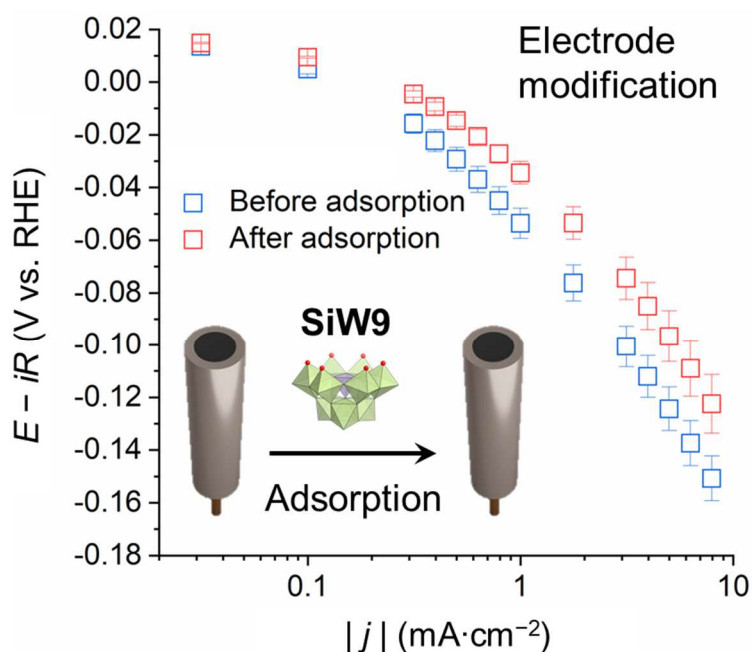


Fig. S13 Tafel plots of the Ru/Vulcan/GC RDE electrode before (blue) and after (red) the modification with **SiW9** in an aqueous buffer solution at pH 10.5 (3 mol kg^{-1} K-carbonate buffer) at 80 °C with H_2 bubbling, based on chronopotentiometry measurements. The loading amount of Ru on RDE is $2.5 \mu\text{g cm}^{-2}$.

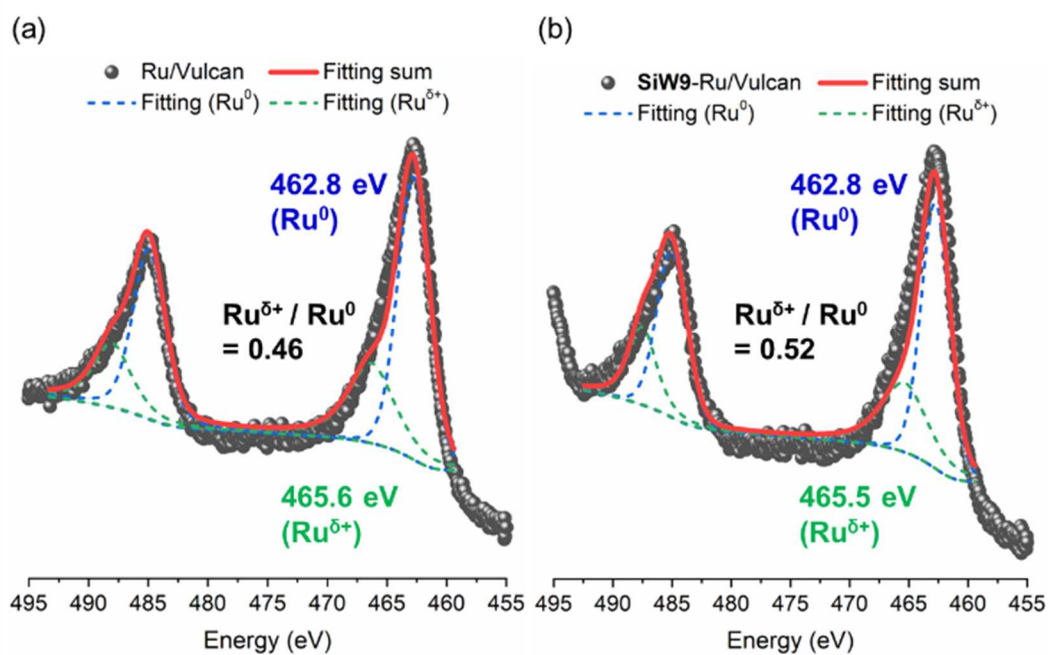


Fig. S14 XPS spectra of Ru 3p orbital for (a) Ru/Vulcan and (b) **SiW9**-Ru/Vulcan.

Supplementary Tables

Table S1 Elemental analysis results of Pt/Vulcan and **SiW9**-Pt/Vulcan, in which Pt/W and Na were confirmed by ICP-AES and AAS analysis, respectively.

	Pt (wt%)	W (wt%)	Na (wt%)	SiW9 : Pt (mol)
Pt/Vulcan	18.6	<0.1	<0.1	–
SiW9 -Pt/Vulcan	17.4	4.5	0.8	3.1 : 100

Table S2 ICP-AES results of **SiW12**-Pt/Vulcan and **Nb6**-Pt/Vulcan.

	Pt (wt%)	W or Nb (wt%)	POM : Pt (mol)
SiW12 -Pt/Vulcan	18.5	<0.1	<i>Not adsorped</i>
Nb6 -Pt/Vulcan	18.6	<0.1	<i>Not adsorped</i>

Table S3 ICP-AES results of electrolyte solution containing **SiW9**-Pt/Vulcan with time.

	0 h	0.5 h	1 h	2 h
Pt (wt%)	<0.1	<0.1	<0.1	<0.1
W (wt%)	<0.1	<0.1	<0.1	<0.1

References

- [S1] K. Xia, T. Yatabe, K. Yonesato, T. Yabe, S. Kikkawa, S. Yamazoe, A. Nakata, K. Yamaguchi, K. Suzuki, “Supported anionic gold nanoparticle catalysts modified using highly negatively charged multivacant polyoxometalates” *Angew. Chem. Int. Ed.* **61**, e202205873 (2022).
- [S2] A. P. Ginsberg, Ed. *Inorg. Synth.* **1990**, 27, 87–94
- [S3] H. Shen, Y. Huang, P. Zhao, R. Gao, Z. Wei, X. Gao, M. Liao, W. Dai, X. Liu, D. Sui, J. Liu, S. Zhu and Y. Wei, *Adv. Funct. Mater.* 2026, **36**, e14862.
- [S4] T. Suzuki, T. Yabe, K. Wachi, K. Yonesato, K. Suzuki, K. Yamaguchi, *ChemNanoMat* **2023**, 9, e202200428.