

Supporting Information

1. Experimental Section

1.1 Catalyst Synthesis

100 mg K_2PtCl_6 (A. R., Shanghai yuanye Bio-Technology Co., Ltd), 132 mg CaH_2 (A. R., Beijing HongHu LianHe HuaGong ChanPin Co.,Ltd), 1000 mg KCl (A. R., Xilong Scientific Co., Ltd.) and 350 mg EC300J (Lion Corporation) conductive carbon black were mixed by Planetary ball-milling (PULVERSETTE 5, Beijing Fritsch Scientific Instruments Co., Ltd.) for 5 h at a speed of 250 rpm in Ar atmosphere in a home-designed stainless steel milling vessel. WC balls with 8 mm diameter are used with balls to powder ratio of 40:1. The ball-milled product is loaded into a quartz tube and then transfer to a tube furnace (SK-G03123K, Tianjin Zhonghuan Electric Furnace Co., Ltd.). The sample is heated to a certain temperature at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in the Ar atmosphere (99.999%, 50 sccm) and held at the highest temperature for 2 h. After cooling to room temperature under Ar flow, the product is washed with 100 mL of acetic acid solution (0.5 wt.%) under Ar protection. Then, the product is washed with deionized water 3 times and ethanol another 2 times, and dried in vacuum at $60\text{ }^\circ\text{C}$.

A control sample was prepared at $500\text{ }^\circ\text{C}$ in H_2 using a mixture of carbon powder, K_2PtCl_6 and KCl after ball milling, using the same method of Pt_2Ca/C . The sample was also washed with deionized water 3 times and ethanol another 2 times, and dried in vacuum at $60\text{ }^\circ\text{C}$, which is designated as Pt-thermal/C.

Pt_2Ca/Ca sample after 10,000 CV cycling in 0.1 M $HClO_4$ is labeled as Pt-leach/C.

Commercial 10% Pt/C was obtained from Shanghai Hesun Co., Ltd.

1.2 Physical Characterization

PXRD: The crystalline phase structure of the samples is obtained by polycrystalline X-ray diffraction (PXRD, Powder X-ray diffractometer, X-Pert3 Powder, PANalytical, $Cu\ K\alpha$).

ICP-AES: The catalyst metal content is determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Inductively Coupled Plasma-Atomic Emission Spectrometer, Prodigy 7, Leeman). The samples are first digested with nitric acid and hydrochloric acid (Microwave Digestion System, UltraWAVE ECR, Milestone), after which the clarified liquid samples are diluted and tested.

XPS: The catalyst surface information is obtained by X-ray Photoelectron spectroscopy (XPS, X-ray Photoelectron Spectrometer, Axis Supra, Kratos Analytical, $Al\ K\alpha$).

HRTEM & HADDF-STEM: The sample morphology and structure are obtained by High-Resolution Transmission Electron Microscopy and High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (Field-emission High-Resolution

Transmission Electron Microscope, JEM-2100F, JEOL, and Spherical Aberration-Corrected Transmission Electron Microscope, Titan Cubed Themis G2 200, FEI).

EDX: The element distribution maps of the sample are obtained by Energy Dispersive X-ray spectroscopy (EDS, Energy Dispersive Spectrometer, Oxford X-Max80 TSR, Oxford Instruments).

1.3 Electrochemical Measurement

1 mg catalyst is dispersed in a mixture of 100 μL ethanol, 100 μL isopropanol, and 10 μL Nafion solution (Shanghai Hesen, 5 wt.%) and sonicated for 30 min to yield an ink. Then 7.8 μL of catalyst ink is dropped onto the working electrode (RDE, $d = 5$ mm, Pine Research Instrumentation, USA) and dried naturally. The catalyst loading is 20 $\mu\text{g}_{\text{Pt}}\cdot\text{cm}^{-2}$.

The electrochemical measurement is carried out in a standard three-electrode system using a CHI 660E electrochemical workstation (CH Instruments). A rotating disc electrode system (Pine Research Instrumentation) is used as the working electrode, a saturated Ag/AgCl electrode (Tianjin Aida Hensheng) is used as the reference electrode, and a 1 cm^2 platinum foil (Tianjin Aida Hensheng) is used as the counter electrode.

Before the ORR test, cyclic voltammetry is first carried out in an Ar-saturated 0.1 M HClO_4 solution at a rate of 250 $\text{mV}\cdot\text{s}^{-1}$ in the range of 0.500 ~ 1.000 V vs. RHE until the curve no longer changes. The background curve is obtained at a scan rate of 10 $\text{mV}\cdot\text{s}^{-1}$ and in the range of 0.050 ~ 1.050 V vs. RHE in the Ar-saturated solution.

After that, the cyclic voltammetric test is performed in an O_2 -saturated 0.1 M HClO_4 solution with 1600 rpm and 10 $\text{mV}\cdot\text{s}^{-1}$. IR correction is applied to the curves, and the resistance at 0.500 V in an Ar-saturated solution is used.

Electrochemical surface area (ECSA) is measured by Cu stripping.¹ The working electrode is first maintained at 1.000 V vs RHE for 120 s in a 0.5 M H_2SO_4 solution with 2.0 $\text{mmol}\cdot\text{L}^{-1}$ CuSO_4 to oxidize any species that might be adsorbed on the surface. Then let the working electrode be maintained at 0.300 V vs RHE for 120 s to underpotential deposited Cu. Then the linear sweep voltammetric is carried out at 2 $\text{mV}\cdot\text{s}^{-1}$ for 0.300 ~ 1.000 V vs. RHE. The background curve is obtained in the same way in 0.5 M H_2SO_4 without Cu ions. The underpotential deposition of Cu ions requires two electrons. Subtract the background from the current curve in the Cu solution, and integrate with respect to time to obtain the charge of associated monolayer Cu. The average value for the charge required to form the monolayer of hydrogen atoms of polycrystalline platinum is 210 $\mu\text{C}\cdot\text{cm}^{-2}$. Thus, the ECSA of the sample can be calculated.

1.4 Computational method

We have employed the Vienna Ab Initio Package (VASP)² to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE³ formulation. We have chosen the projected augmented wave (PAW) potentials⁴ to describe the ionic cores and take valence electrons into account

using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-5} eV. A geometry optimization was considered convergent when the force change was smaller than $0.02 \text{ eV}\cdot\text{\AA}^{-1}$. Grimme's DFT-D3 methodology⁵ was used to describe the dispersion interactions.

The equilibrium lattice constant of fcc Pt unit cell was optimized, when using a $10\times 10\times 10$ Monkhorst-Pack k-point grid for Brillouin zone sampling, to be $a = 3.919 \text{ \AA}$. We then use it to construct a Pt(111) surface model (model 1) with $p(4\times 4)$ periodicity in the x and y directions and 4 atomic layers in the z direction separated by a vacuum layer in the depth of 15 \AA in order to separate the surface slab from its periodic duplicates. This surface model contains 64 Pt atoms. During structural optimizations, the gamma point in the Brillouin zone was used for k-point sampling, and the bottom two stoichiometric layers were fixed while the top two were allowed to relax.

The equilibrium lattice constant of cubic Pt_2Ca unit cell was optimized, when using a $5\times 5\times 5$ Monkhorst-Pack k-point grid for Brillouin zone sampling, to be $a = 7.620 \text{ \AA}$. We then use it to construct a $\text{Pt}_2\text{Ca}(111)$ surface model (model 2) with $p(2\times 2)$ periodicity in the x and y directions and 2 stoichiometric layers in the z direction separated by a vacuum layer in the depth of 15 \AA in order to separate the surface slab from its periodic duplicates. This surface model contains 16 Ca and 32 Pt atoms. During structural optimizations, the gamma point in the Brillouin zone was used for k-point sampling, and the bottom stoichiometric layer was fixed while the top one was allowed to relax.

The heterojunction surface model (model 3) was built by adding two Pt atomic layers from model 1 to the top of model 2. The mismatch between the two Pt atomic layers and two Pt_2Ca stoichiometric layers is as small as 2.8%. During structural optimizations, the gamma point in the Brillouin zone was used for k-point sampling, and the Pt_2Ca part was fixed while the two Pt atomic layers were allowed to relax.

The free energy of a gas phase molecule or an adsorbate on the surface was calculated by the equation $G = E + \text{ZPE} - TS$, where E is the total energy, ZPE is the zero-point energy, T is the temperature in Kelvin (298.15 K is set here), and S is the entropy.

References

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2. Further analysis

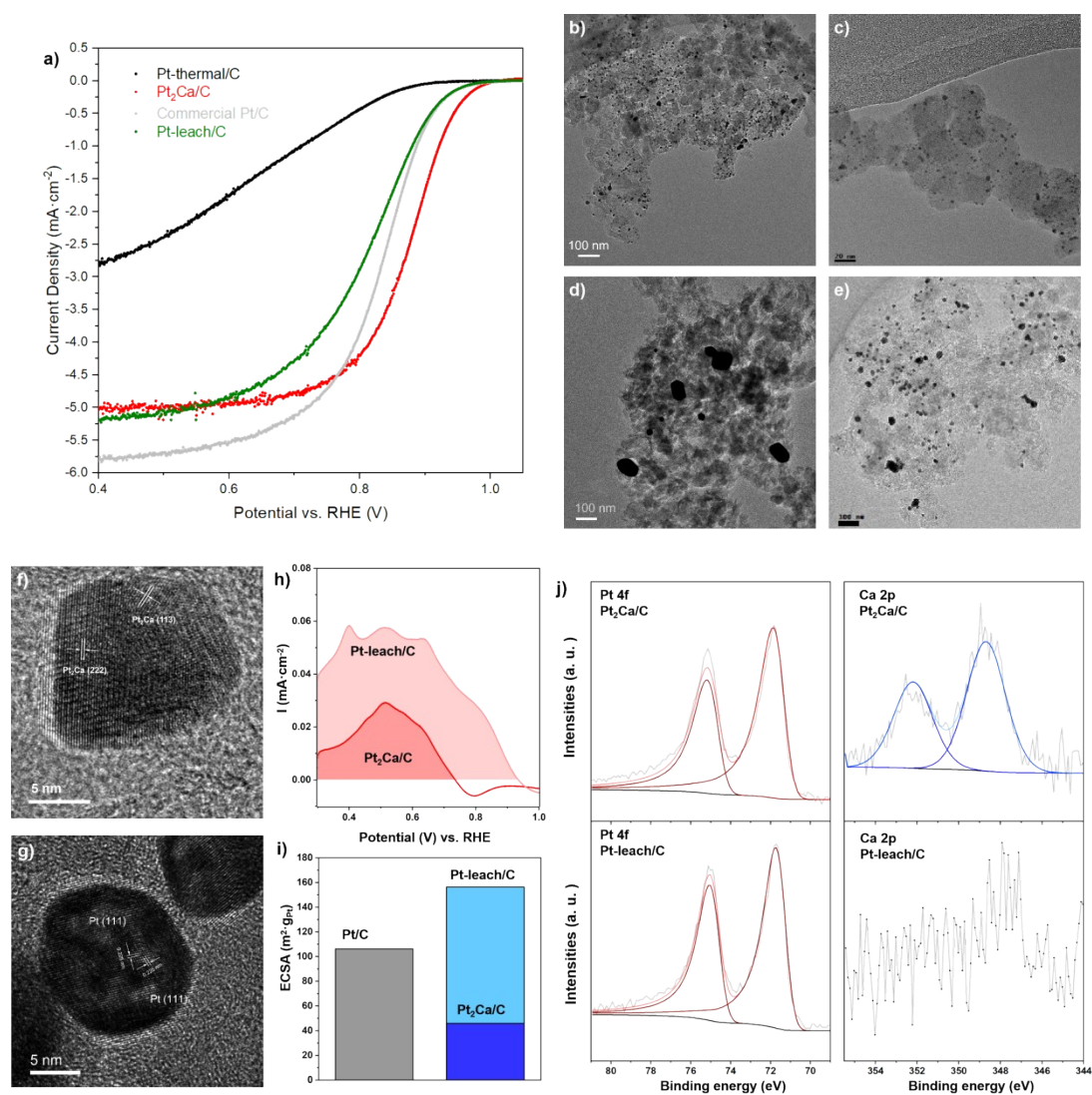


Fig. S1 (a) LSV curve of Pt₂Ca/C, commercial Pt/C and Pt-thermal/C in 0.1 M HClO₄ and TEM image of (b) Pt₂Ca/C obtained at 500 °C; (c) Commercial Pt/C; (d) Pt-thermal/C; (e) Pt-leach/C; HRTEM image of (f) Pt₂Ca/C; (g) Pt-leach/C; (h) Cu stripping curves of Pt₂Ca/C and Pt-leach/C; (i) ECSA of Pt/C, Pt₂Ca/C and Pt-leach/C; (j) XPS of Pt₂Ca/C and Pt-leach/C

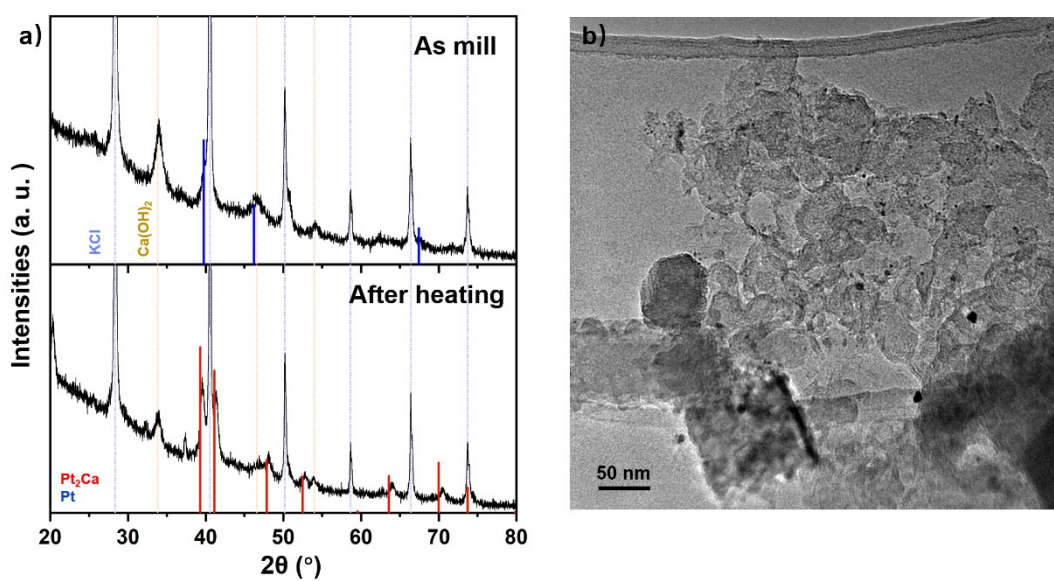


Fig. S2 (a) XRD patterns of the sample after ball milling and after heating; (b) TEM image of precursor after ball milling.

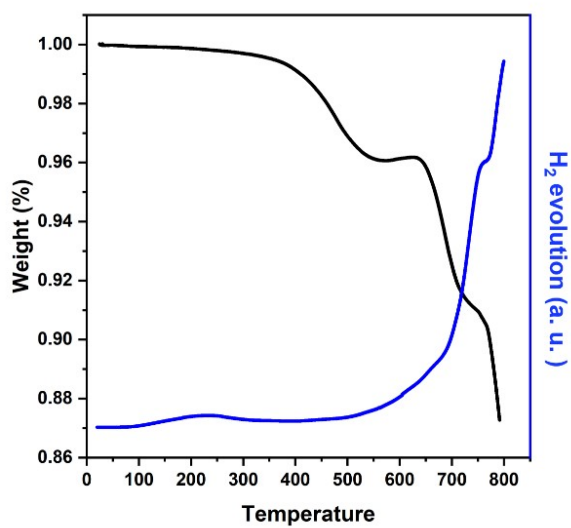


Fig. S3 TG and TPD of mixture of KCl-CaH₂.

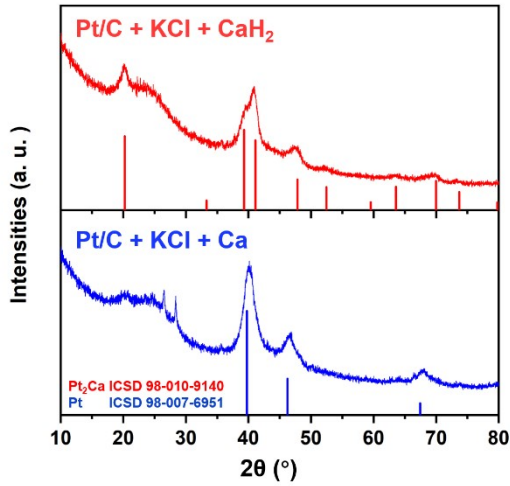


Fig. S4 XRD patterns of Pt/C-KCl-CaH₂ and Pt/C-KCl-Ca mixture after reaction under 400 °C.



Fig. S5 optical photograph of KCl-CaH₂ mixture after heated at 600 °C (left) and 400 °C (right) for 2 h, respectively. We press the mixture into a disk under 10 MPa, and the support is graphite. The picture shows that the mixture has no signal of melting under 400 °C, while obviously melting at 600 °C.

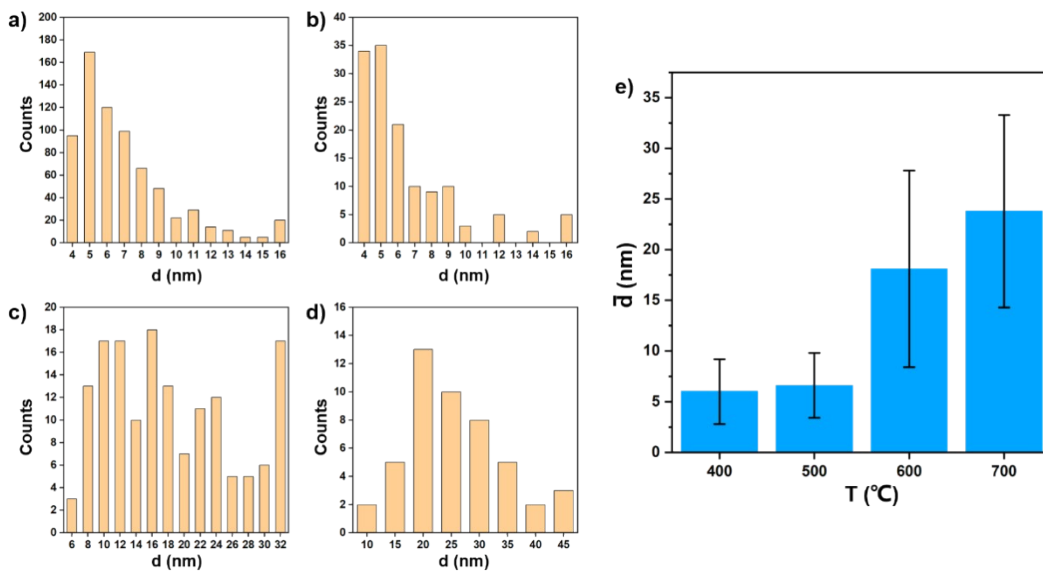


Fig. S6 (a-d) Statistical histogram of particle size of samples heated in 400, 500, 600, and 700 °C. (e) Diagram of average particle size changing with reaction temperature.