Supplementary Materials for

Grain-boundary-rich Pt nanoparticle assembly for catalytic hydrogen sensing at room temperature

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Materials and Methods

Material synthesis

Preparation of Pt NPs. Pt NPs were synthesized using a previously reported method with slight modifications \( (1) \). Specifically, 35 mL aqueous solution of 0.14 mmol hydrogen hexachloroplatinate (IV) hexahydrate \( (\text{H}_2\text{PtCl}_6, \text{Sigma Aldrich}) \) was added to 460 mL of DI water at 100°C. One minute later, 11.6 mL aqueous solution of 0.42 mmol sodium citrate tribasic dihydrate \( (\text{C}_6\text{H}_{9}\text{Na}_3\text{O}_9, \text{Sigma Aldrich}) \) was added. After one minute, 5 mL of the freshly prepared ice-cold aqueous mixed solution of 0.14 mmol sodium borohydride \( (\text{NaBH}_4, \text{Sigma Aldrich}) \) and 0.28 mmol \( \text{C}_6\text{H}_{9}\text{Na}_3\text{O}_9 \). After ten minutes, the grayish-brown solution was cooled down to room temperature naturally. Before electrochemical NP assembly, the as-synthesized 500 mL Pt NP solution was concentrated using a rotary evaporator at 75°C by 10-fold to a final volume of 50 mL and Pt NP concentration of \( \sim 1.7 \) μM.

Electrochemical synthesis of wet Pt NP assemblies. A three-electrode system was utilized to synthesize Pt NP assemblies by linking Pt NPs into Pt NP networks. A Pt foil \( (~240 \text{ mm}^2) \), a Pt foil \( (~385 \text{ mm}^2) \), and an Ag/AgCl in saturated KCl aqueous solution were used as the working, counter, and reference electrodes, respectively. Prior to electrochemical synthesis, two Pt foils were electrochemically polished in 0.5 M H\(_2\)SO\(_4\) aqueous solution by cycling the electrode potential between 1.1 V and −0.23 V at a sweep rate of 0.1 V/s for 500 cycles using a CHI 650E potentiostat. The Ag/AgCl reference electrode and two Pt foils were rinsed using DI water several times. In a typical experiment, 8 mL of concentrated Pt NP solution was added to a 10 mL glass beaker. A constant electrode potential of -2 V was applied at the working electrode for five hours until the supernatant color turned clear, indicating the completion of NP assembly. Finally, the supernatant was carefully removed using a pipette, and the wet Pt NP assemblies at the bottom were washed with DI water ten times in one week.

Preparation of dry Pt NP assemblies. Critical Point Drying (CPD) was employed to prepare a dry Pt NP assembly powder from wet Pt NP assembly. Before CPD, the solvent in wet Pt NP assemblies was exchanged from DI water to acetone by removing the supernatant carefully. This solvent exchange step was repeated three times a day for one week. Next, the wet Pt NP assemblies were supercritically dried using an SPI-DRY model CO\(_2\) critical point dryer with a recirculating water bath (ISOTEMP 10065). The acetone was first completely replaced with liquid CO\(_2\) at 18°C, and liquid CO\(_2\) was evaporated by raising the temperature to 37°C. Thirty minutes later, the CPD process was completed, and dry Pt NP assemblies were obtained.

Characterization

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were taken using JEOL 3100R05 TEM (Double Cs Corrected TEM/STEM) and Thermo Fisher Titan (probe Cs Corrected TEM, 300 kV). HRTEM images were collected using Thermo Fisher Titan (imaging Cs Corrected TEM, 300 kV). The particle size distribution was estimated
using Nano Measurer 1.2 software. The high-resolution XRD data were collected at the 11-BM-B beamline at the Advanced Photon Source (APS), Argonne National Laboratory. The chemical state and elementary ratio were analyzed by X-ray Photoelectron Spectroscopy (XPS, ThermoFisher Scientific NEXSA UV and X-ray Photoelectron Spectrometer). XPS peaks were calibrated according to the C 1s peak at 284.8 eV and fitted using a composite function (30% Lorentzian + 70% Gaussian) using the Avantage software. Steady-state X-ray absorption spectroscopy (XAS) measurement was performed at 12-BM beamline at the Advanced Photon Source (APS), Argonne National Laboratory. The XAS data were collected under room temperature with fluorescence mode using a 13-element germanium solid-state detector. Three ion chambers were used. One of them was placed before the sample for the incident X-ray flux reference signal. The other two ion chambers (second and third chambers) are placed after the sample. The Pt foil is placed between the second and third ion chambers and used for collecting Pt metal XAS spectrum for energy calibration.

Analysis of GBs and d spacings

HRTEM images were processed using ImageJ software. After obtaining a Fast-Fourier transform (FFT) of images, \{111\} and \{200\} planes were identified. If there is a GB, \{111\} and \{200\} planes for both grains were identified. GB types were determined by the orientations of two grains with respect to each other. Among 58 GBs that are identified with HRTEM and STEM images, we observed 53 examples of \(\Sigma 3\) GBs, 3 examples of \(\Sigma 11\) GBs, and two possible \((111)/(200)\) GBs.

Line profiles across \{111\} and \{200\} planes were obtained in multiple positions of the particles or the grains. The peak positions of the line profiles are identified with the plots from the OriginPro program. By comparing the peak positions and the images, \(d\)-spacings were obtained for both \{111\} and \{200\} planes. To compare \(d\)-spacing distributions between Pt NPs and Pt NP assembly, we took images with the same magnification and same microscope so that the pixel sizes of the images for both samples were identical. 22 Pt NPs (9 cases at pixel size = 0.0149 nm; 13 cases at pixel size = 0.020 nm) and 23 Pt NP assemblies (12 cases at pixel size = 0.0149 nm; 11 cases at pixel size = 0.020 nm) were analyzed. The histograms of \(d\)-spacing distribution for \{111\} and \{200\} planes of both Pt NP and Pt NP assembly were plotted with the bin size of 0.015 nm (Fig. 3G) and 0.020 nm (fig. S16), similar to the pixel sizes of these images. In both cases, the average \(d\)-spacings for Pt NP and Pt NP assembly are similar, but the standard deviations of Pt NP assembly are larger than that of Pt NP (for pixel size = 0.0149 nm, standard deviation for \{111\}: 0.021 vs 0.017 nm, standard deviation for \{200\}: 0.019 vs 0.015 nm; for pixel sizes = 0.020 nm, standard deviation for \{111\}: 0.028 vs 0.021 nm, standard deviation for \{200\}: 0.026 vs 0.021 nm). The stain mapping of the HR-STEM images was obtained using an open-source program, Strain++, which is based on a geometric phase analysis (GPA) algorithm as detailed in the paper by Martin Hýtch et al.(2)

\(\text{H}_2\) sensor fabrication
Six commercially available thermometers, including a J-type thermocouple wire (NEW Keysight Agilent, Part number: 34970-61606, Measuring range: -40°C~750°C), a K-type thermocouple wire (Adafruit, Part number: 270, Measuring range: -40°C~500°C) and a liquid-in-glass thermometer (SP Bel-Art, Part number: 13-201-663, Measuring range: -20°C~110°C), a cooking thermometer (Pilita, Part number: DT-68, Measuring range: -50°C~300°C), a digital pocket thermometer (UEi Test Instruments, Part number: PDT650, Measuring range: -50°C~300°C) and a thermistor (Adafruit, Part number: 3915, Measuring range: -20°C~120°C) were used to prepare catalytic H₂ sensors. A wet slurry containing 1 mg Pt NP assembly (prepared by mixing 1 mg Pt NP assembly with 100 μL ethanol) was drop-casted on the sensing region of a thermometer followed by drying in air.

In the control experiments using other Pt catalysts, 1 mg of Pt NPs (precipitated by centrifuge), Pt NPs without ligand (precipitated by adding NaOH aqueous solution until pH reaches14), Pt black (Sigma Aldrich), Pt powder (Sigma Aldrich), and Adams’ catalyst (Sigma Aldrich) were dispersed in 100 μL ethanol to prepare their corresponding slurries. The obtained slurries were drop-casted on the tip of a J-type thermocouple wire followed by drying in air.

**Gas sensing tests**
The standard H₂ sensing tests in this study were carried out using sensors prepared from a J-type thermocouple wire (abbreviated as J-H₂ sensors) unless otherwise specified.

**Standard H₂ sensing test protocol.** The H₂ sensing tests were carried out using a home-built apparatus at room temperature, which includes two gas cylinders (synthetic air and H₂ from Airgas Co., Ltd) and mass flow controllers, a data acquisition meter (Keysight/Agilent 34972A LXI) for real-time recording of the temperature readout, and PC Computer (Hewlett-Packard Co., Ltd) for storing data (3). A J-H₂ sensor was placed directly in front of the gas outlet during the test (Fig. 2A insert). Before exposure to H₂, the J-H₂ sensor was first stabilized in synthetic air (21% O₂+79% N₂) at a flow rate of 1000 sccm at room temperature and relative humidity of 0%. Then, H₂ gas was mixed with synthetic air to achieve various H₂ concentrations of 4%, 3%, 2%, 1%, 0.5%, 0.25%, 0.1%, and 0.05%. These H₂/air mixtures sequentially flowed over the J-H₂ sensor at a constant rate of 1000 sccm to obtain the response/recovery curves of J-H₂ sensors.

**Interference/cross-sensitivity test.** Thirty-six interference gases were tested, including carbon monoxide, hydrogen sulfide (Airgas Co., Ltd), sulfur dioxide (Airgas Co., Ltd), nitrogen dioxide (Airgas Co., Ltd), ethylene (Airgas Co., Ltd), natural gas (Ardent Natural Gas, LLC), ammonia (Sigma Aldrich), formaldehyde (Sigma Aldrich), acetonitrile (Sigma Aldrich), isopropanol (Sigma Aldrich), methanol (Sigma Aldrich), ethanol (Sigma Aldrich), acetone (Sigma Aldrich), hexane (Sigma Aldrich), heptane (Sigma Aldrich), octane (Sigma Aldrich), benzene (Sigma Aldrich), toluene (Sigma Aldrich), xylenes (Sigma Aldrich), ethyl acetate (Sigma Aldrich), petroleum ether (Sigma Aldrich), isopropylmethyl ketone (Sigma Aldrich), 1-butanol (Sigma Aldrich), n-octyl
ether (Sigma Aldrich), cyclohexane (Sigma Aldrich), cyclohexanone (Sigma Aldrich), diethyl ether (Sigma Aldrich), butylamine (Sigma Aldrich), trifluorotoluene (Sigma Aldrich), tetrahydrofuran (Sigma Aldrich), nitromethane (Sigma Aldrich), propionitrile (Sigma Aldrich), dimethyl sulfoxide (Sigma Aldrich), N,N-dimethylformamide (Sigma Aldrich), methylacetoacetate (Sigma Aldrich), tetraethylene glycol (Sigma Aldrich). The concentration for most of the interference gases was 4%, except H$_2$S (0.4 ppm), NO$_2$ (4 ppm), SO$_2$ (4 ppm), ethylene (40 ppm). For those interference gases bought from Airgas Co., Ltd (CO, H$_2$S, SO$_2$, NO$_2$, ethylene) and natural gas, the concentrations were regulated by varying the flow rate ratio of synthetic air and interference gases. As to others purchased from Sigma Aldrich (highly purity of liquids), the concentrations were adjusted by the flow rate ratio of pure air and air bubbling through corresponding liquids.

**First-principles calculations.**
All DFT calculations were performed using the Vienna ab initio simulation package (VASP) (4, 5). Core electrons were described using the projected-augmented wave (PAW) method (6). The Kohn-Sham wave functions were expanded on a plane-wave basis with a kinetic energy cutoff of 400 eV to describe valence electrons. The generalized gradient approximation using the Perdew-Burke-Ernzerhof functional was employed to evaluate the exchange-correlation energy (7).

The Pt surface was modeled as a four-layer ($\sqrt{3} \times 2$) Pt (111) slab. The bottom two layers of Pt (111) surface were kept frozen, while the other layers and adsorbed molecules were set free to relax. A vacuum space of 14 Å was added to all surface models to ensure no appreciable interaction between periodic images. The Monkhorst-Pack scheme was employed to sample the Brillouin zone using a $5 \times 5 \times 1$ k-point grid for atomic structure optimization (8). For Pt$_{201}$ NP and Pt$_{383}$ Σ3 [110] (111) GB models, a vacuum space of > 15 Å was added to prevent any appreciable interaction between periodic images. The Brillouin zone was sampled only on Gamma point for the geometry optimization. All geometries were considered optimized when the force on each atom was < 0.03 eV/Å. The location and energy of transition states were calculated with the climbing-image nudged elastic band method (9, 10).

**Strain analysis.**
The change of lattice matching near the GB leads to a substantial strain on the Pt-Pt bonds. Strain analysis of Pt Σ3 [110] (111) GB is carried out based on the DFT optimized models. A number of studies have shown that Pt (111) surface is more active than Pt (100) and Pt (110) for the hydrogen oxidation reaction (11, 12), and is the dominant facet of Pt NP (13, 14). Thus, strain analysis and subsequent investigation of reaction activity in this work are mainly focused on Pt (111) facets.

The strain of surface atoms at the Pt GB was calculated by the following equation:

$$\epsilon_i = \frac{\overline{d_i} - d_{np,(111)}}{d_{np,(111)}} \times 100\% \quad (1)$$

where $\overline{d_i}$ is the average Pt-Pt bond length between the atom $i$ and its neighboring surface atoms, $d_{np,(111)}$ is the average Pt-Pt bond length of (111) facet in Pt NP.
For the Pt$\text{201}$ NP, $d_{np,(111)}$ was calculated to be 2.717 Å. For the Pt$\text{383} \Sigma 3$ [110] (111) GB formed by two Pt$\text{201}$ NPs, the average Pt-Pt bond length of the GB atoms along (111) plane was calculated to be 2.764 Å, i.e. a tensile strain of +1.73% with reference to Pt$\text{201}$ NP (111) facet, according to the Eq. (1).

**Micro-kinetic model for H$_2$ oxidation reaction over Pt**

There are two primary hydrogen oxidation mechanisms on Pt (111) surface: associative and dissociative pathways (15). We have considered both mechanisms and built the corresponding micro-kinetic models.

1. **Associative pathway**

   For associative pathway, the H$_2$ oxidation reaction on Pt (111) surface involves the following steps:

   1. $\frac{1}{2} H_2(g) + * \rightleftharpoons H^*$  \hspace{1cm} (R1)
   2. $O_2(g) + * \rightleftharpoons O_2^*$  \hspace{1cm} (R2)
   3. $O_2^* + H^* \rightleftharpoons OOH^* + *$ \hspace{1cm} (R3, rate-determining step)
   4. $OOH^* + H^* \rightleftharpoons 2OH^*$  \hspace{1cm} (R4)
   5. $OH^* + H^* \rightleftharpoons H_2O^* + *$  \hspace{1cm} (R5)
   6. $H_2O^* \rightleftharpoons H_2O(g) + ^*$  \hspace{1cm} (R6)

   Based on the rate-limiting step approximation (R3), we can derive the coverage of H, O$_2$, H$_2$O, OH and OOH as follows:

   \[
   \theta_H = K_1 p_{H_2}^{1/2} \theta_* \hspace{1cm} (2)
   \]

   \[
   \theta_{O_2} = K_2 p_{O_2} \theta_* \hspace{1cm} (3)
   \]

   \[
   \theta_{H_2O} = \frac{p_{H_2O}}{K_6} \theta_* \hspace{1cm} (4)
   \]

   \[
   \theta_{OH} = \frac{p_{H_2O}}{K_1 K_5 K_6 p_{H_2}^{1/2}} \theta_* \hspace{1cm} (5)
   \]

   \[
   \theta_{OOH} = \frac{p_{H_2O}^2}{K_1^2 K_4 K_5^2 K_6^2 p_{H_2}^{3/2}} \theta_* \hspace{1cm} (6)
   \]

   where the $\theta_*$ is the coverage of open sites. After applying the site conservation rule (Eq. 7),

   \[
   \theta_* + \theta_H + \theta_{O_2} + \theta_{OH} + \theta_{OOH} + \theta_{H_2O} = 1 \hspace{1cm} (7)
   \]

   we derive the coverage of open sites as:

   \[
   \theta_* = \frac{1}{1 + K_1 p_{H_2}^{1/2} + K_2 p_{O_2} + \frac{p_{H_2O}}{K_1 K_5 K_6 p_{H_2}^{1/2}} + \frac{p_{H_2O}^2}{K_1 K_4 K_5 K_6^2 p_{H_2}^{3/2}} + \frac{p_{H_2O}}{K_6}} \hspace{1cm} (8)
   \]

   The rate of H$_2$ oxidation is then written as:
\[ R = R_3 = k_3^+ \theta_{O_2} \theta_H (1 - \gamma) \] (9)

where \( k_3^+ \) is the forward rate constant for \( R_3 \), which can be obtained as Eq. (10); \( K_i \) is the equilibrium constants for \( R_i \), which are calculated using Eq. (11); \( p_{H_2}, p_{O_2} \) and \( p_{H_2O} \) are the partial pressures of \( H_2, O_2 \) and \( H_2O \), which are listed in Table S3; the approach to equilibrium \( \gamma \) can be obtained by using Eqs. (12) and (13).

\[ k_3^+ = \frac{k_BT}{h} e^{-(G_3^{TS} - G_3^s)/k_BT} = \frac{k_BT}{h} e^{-(E_{a,3})/k_BT} \] (10)

\[ K_i = e^{-\Delta G_i/k_BT} = e^{-\left(\Delta E_i + \Delta ZPE_i - T\Delta S_i\right)/k_BT} \] (11)

\[ \gamma = \prod_i \gamma_i^{n_i} = \gamma_3 = \frac{p_{H_2O}^2}{K_{eq} p_{H_2}^2 p_{O_2}} \] (12)

\[ K_{eq} = \prod_i K_i^{n_i} = K_1^4 K_2 K_3 K_4 K_5^2 K_6^2 \] (13)

where \( E_{a,3} \) is the activation energy barrier of \( R_3 \) (Table S1), \( \Delta E_i \) is the reaction energy of \( R_i \) (Table S1), \( \Delta ZPE_i \) and \( T\Delta S_i \) are the correction of zero-point energy and entropy of \( R_i \), respectively (Table S4).

2. Dissociative pathway

For the dissociative pathway, we assume the following elementary steps:

\[
\begin{align*}
1/2 \text{H}_2(g) + * & \rightleftharpoons \text{H}^* \\
\text{O}_2(g) + * & \rightleftharpoons \text{O}_2^* \\
\text{O}_2^* + * & \rightleftharpoons 20^* \\
\text{O}^* + \text{H}^* & \rightleftharpoons \text{OH}^* + * \\
\text{OH}^* + \text{H}^* & \rightleftharpoons \text{H}_2\text{O}^* + * \\
\text{H}_2\text{O}^* & \rightleftharpoons \text{H}_2\text{O(g)} + *
\end{align*}
\]

(R1) (R2) (R3) (R4) (R5) (R6)

Based on the rate-limiting step approximation (R4), we can derive the coverage of \( H, O_2, O, H_2O, \) and \( OH \) as follows:

\[ \theta_H = K_1 p_{H_2}^{1/2} \theta_* \] (14)

\[ \theta_{O_2} = K_2 p_{O_2} \theta_* \] (15)

\[ \theta_O = \sqrt{K_2 K_3 p_{O_2}} \theta_* \] (16)

\[ \theta_{H_2O} = \frac{p_{H_2O}}{K_6} \theta_* \] (17)

\[ \theta_{OH} = \frac{p_{H_2O}}{K_1 K_5 K_6 p_{H_2}^{1/2}} \theta_* \] (18)

where the \( \theta_* \) is the coverage of open sites. After applying the site conservation rule (Eq. 19),

\[ \theta_* + \theta_H + \theta_{O_2} + \theta_O + \theta_{H_2O} + \theta_{OH} = 1 \] (19)
we derive the coverage of open sites as:
\[
\theta_s = \frac{1}{1 + K_1 p_{H_2}^{1/2} + K_2 p_O + \sqrt{K_2 K_3 p_O} + \frac{p_{H_2 O}}{K_6} + \frac{p_{H_2 O}}{K_1 K_5 K_6 p_{H_2}^{1/2}}}
\] (20)

The rate of H₂ oxidation can be written as:
\[
R = 2R_4 = 2k_4^+ \theta_O \theta_H (1 - \sqrt{\gamma})
\] (21)

where \(k_4^+\) is the forward rate constant for R4, which can be obtained as Eq. (22); \(K_i\) is the equilibrium constants for R_i, which are calculated as Eq. (11); \(p_{H_2}, p_O\) and \(p_{H_2 O}\) are the partial pressures of H₂, O₂, and H₂O, which are listed in Table S3; the approach to equilibrium \(\gamma\) can be obtained by Eqs (23) and (24).

\[
k_4^+ = \frac{k_B T}{h} e^{-(E_{a,4}^{TS} - G_4^*)/k_B T} = \frac{k_B T}{h} e^{-(E_{a,4})/k_B T}
\] (22)

\[
\gamma = \prod_i \gamma_i = \gamma_4^2 = \frac{p_{H_2 O}^2}{K_{eq} p_{H_2}^2 p_O}
\] (23)

\[
K_{eq} = \prod_i K_i^{n_i} = K_1 K_2 K_3 K_4 K_5 K_6
\] (24)

where \(E_{a,4}\) is the activation energy barrier of R4 (Table S2), \(\Delta E_i\) is the reaction energy of R_i (Table S2).

**Rate calculation of Pt Σ3 [110] (111) GB**

For Pt (111) slabs with different Pt-Pt bond lengths and (111) facet of Pt_201 NP, the activation energy barriers of O₂ dissociation (0.54~0.72 eV, Table S2) and OH* formation (0.75~1.02 eV, Table S2) are considerably higher than that of OOOH* formation (0.38~0.42 eV, Table S1). Thus, the associative pathway is the dominant reaction path on NP (111) facet (Fig. 4C). Micro-kinetic modeling also suggests that the coverage of H⁺ (\(\theta_H\)) is close to 1. In other words, (111) facet is mostly covered by H⁺.

However, owing to the greatly reduced barrier of O₂ dissociation (0.008 eV, Table S2) and OH* formation (0.60 eV, Table S2), the GB area is mostly covered by O* (\(\theta_O \sim 1\)). Diffusion of H⁺ on Pt (111) surface fast enough, so H⁺ on Pt NP (111) facet can easily diffuse to the GB region and react with O*, creating bifunctional reaction sites near the GB (fig. S22). The maximum rate near Pt GB can be approximated as below:

\[
R_{GB}^{max} = 2k_4^+ \theta_{O,GB} \theta_{H,sur}
\] (25)

where \(\theta_{O,GB}\) is the coverage of O* adsorbed near GB and \(\theta_{H,sur}\) is the coverage of H* adsorbed on Pt NP (111) facet.
We simply counted the number of atoms that are in favor of O binding and H binding to estimate $\theta_{O,GB}$ and $\theta_{H,sur}$. For the Pt$_{383}$ $\Sigma 3$ [110] (111) GB model in fig. S22, the $\theta_{O,GB}$ and $\theta_{H,sur}$ are estimated as:

\[ \theta_{O,GB} = \frac{7}{17} = 0.412 \]  \hspace{1cm} (26)

\[ \theta_{H,sur} = \frac{10}{17} = 0.588 \]  \hspace{1cm} (27)

It is worth noting that different approaches to estimating $\theta_{O,GB}$ and $\theta_{H,sur}$ may change the exact number, but the improvement in the order of magnitude will still hold.

Size effect on the strain distribution near Pt $\Sigma 3$ [110] (111) GB

To gain insight into the size effect on strain distribution near Pt $\Sigma 3$ [110] (111) GB, we built a large Pt$_{405}$ NP model with the same shape as Pt$_{201}$ to construct a Pt$_{783}$ $\Sigma 3$ [110] (111) GB. As shown in fig. S18, the Pt atoms at the GB along the (111) plane also show a tensile strain of 1.88% relative to their counterparts on the (111) facet of an isolated Pt NP.
Fig. S1.

(A) pH as a function of distance from the Pt foil cathode with an area of ~240 mm$^2$ at -2 V vs. Ag/AgCl reference electrode during electrosynthesis of NP assembly. pH values were measured using a micro pH electrode (Thermo Scientific, Product Number: 9863BN). The solution pH value gradually decreased from ~14 near the cathode surface (less than 1 mm) to 5.3 in the bulk solution. (B) High-resolution C1s XPS spectra of Pt NPs, pH=14-treated Pt NPs (Pt NPs were precipitated by adding sodium hydroxide aqueous solution until solution pH reaches 14), and Pt NP assembly. The peak centered at 288 eV belongs to the C=O surface functional group of sodium citrate ligands (16). The results indicate that most sodium citrate ligands were removed from the Pt NP under the electrogenerated highly alkaline environment near the cathode. (C) High-resolution Pt 4f XPS spectra of Pt NPs and Pt NP assembly reveal that no noticeable change in the valence state of Pt occurs during the electrosynthesis process.
**Fig. S2.**

Pt NP assembly driven by water electrolysis. Ex-situ TEM images of Pt NP solution near the cathode as a function of time. After applying a potential of -2 V vs. Ag/AgCl at the cathode for 0 min, 2 min, 5 min, 10 min, 30 min, 45 min, 60 min, 90 min, 120 min, and 180 min, 10 μL of Pt NP solution was sampled from the region that was extremely close to the cathode surface using a pipette at each time point. Then, the collected Pt NP solutions were drop-casted on the TEM grids (Ted Pella, Product Number: 01800-F) and naturally dried in the air before TEM analysis.
Fig. S3.
Identification of a $\Sigma 11$ GB in the Pt NP assembly based on the angles between the Fourier-transform patterns of two crystals.
Fig. S4.
Gram-scale electrosynthesis of Pt NP assembly. Photographs of (A and B) set-up before and after electrochemical synthesis. (C) Wet Pt NP assembly dispersed in DI water. (D) Dry Pt NP assembly powder after critical point drying. (E) Photograph of ~1 gram dry Pt NP assembly powder on a balance. (F and G) TEM images of Pt NP assembly at low and high magnifications. Thirty-five aliquots of diluted 500 mL Pt NP solution (17.5 L in total) were concentrated by ~17 fold to a final volume of ~1000 mL at 75°C using a rotary evaporator in batches. The concentration of the concentrated Pt NP solution was estimated to be ~3 μM. Titanium foils (Sigma Aldrich) were utilized as the counter electrode (120 cm²) and the working electrode (75 cm²). An electrode potential of -2 V was applied at the working electrode for twelve hours until the supernatant color turned clear, and other conditions were the same as milligram-scale synthesis. As shown in TEM images, the gram-scale synthesized gel exhibits similar morphology and size to the milligram-scale ones. Subsequently, the supernatant was carefully removed without disturbing the wet gel at the bottom. The wet gel was washed by DI water ten times and then completely exchanged with acetone in two weeks. Finally, the wet gel immersed in acetone was subjected to Critical Point Drying to prepare dry Pt NP assemblies. Notably, the gel was partially contaminated with titanium oxide due to the oxidation of titanium foil at the anode during the electrochemical synthesis.
Fig. S5.
Photographs of Pt NP assemblies. (A) Wet Pt NP assembly in DI water. (B) Dry Pt NP assembly powder after critical point drying.
**Fig. S6.**

**Electrochemical surface area measurement.** Glassy carbon electrode (GCE, diameter = 3 mm), graphite rod, and Ag/AgCl (sat’d KCl) are used as the working, counter, reference electrodes, respectively. 0.1 M HClO₄ aqueous solution is used as the electrolyte. Prior to use, GCE was consecutively polished by 1 μm, 0.3 μm, and 0.05 μm Al₂O₃ powders and then washed by sonication in 0.1 M H₂SO₄ and 1:1 (v:v) H₂O/ethanol mixture. The Pt black and Pt NP inks were prepared by sonication a mixture of 1 mg Pt material, 4 mg Vulcan carbon, and 1 mL 3:1 (v:v) H₂O-isopropanol (IPA) with 0.05% Nafion for 30 min. The preparation of Pt NP assembly ink was slightly different. Briefly, 1 mg Pt NP assembly powder was added to 1 mL 3:1 (v:v) H₂O-IPA and sonicated for 15 min. Next, 2 mg Vulcan was added to the above suspension and sonicated for another 10 min, followed by adding 10 μL 5% Nafion and another 5 min sonication. Finally, 3 μL of ink was drop-cast by a pipette onto the GCE and dried in air, resulting in a mass loading of 3 μg Pt on the electrode or ~42.5 μg/cm²geo. Cyclic voltammograms of Pt NPs, Pt NP assembly, and Pt black were recorded at a potential window between -0.25 V and 1.0 V at a scanning rate of 50 mV/s. All the measurements were performed three times to obtain the average values with standard deviations.

| Material           | Surface area (cm²/mg) |
|--------------------|-----------------------|
| Pt NP              | 340 ± 24              |
| Pt NP assembly     | 70 ± 1                |
| Pt black           | 144 ± 5               |
Fig. S7.

Catalytic H\textsubscript{2} sensing performance of various Pt materials. Response-recovery curves of a J-type thermocouple coated with 1 mg of various Pt catalysts in response to H\textsubscript{2} at different concentrations (4\%–0.05\%) at room temperature. Pt NPs (precipitated by centrifuge), Pt NPs without ligands (prepared by adjusting the solution pH to 14 using a NaOH solution, see fig. S1), Pt NP assembly, Pt black (Sigma Aldrich), Pt bulk powder (Sigma Aldrich), Adams’ catalyst (Sigma Aldrich) were separately mixed with ethanol to prepare a catalyst slurry which was drop-casted on the tip of J-type thermocouple, followed by drying under the ambient condition to prepare the catalytic H\textsubscript{2} sensors.
Fig. S8.

**One-second H₂ sensing test. (A)** Temperature variations of a Pt NP assembly sensor in response to 1-second-long pulses of H₂ with various concentrations from 4% to 0.05% for 23 cycles. (B) Expanded view of the first cycle result, and (C) Statistics of sensor temperatures at different H₂ concentrations at an exposure time of 1 s.
Fig. S9.
Operating temperature(A) and humidity(D) dependence tests. High ambient temperatures (50°C and 80°C) were created by heating the sensing test Teflon chamber (B) where the J-type thermocouple was housed, while the ultra-low temperature of -30°C was achieved by placing dry ice around the testing chamber (C). The catalytic H₂ sensor was exposed to a step-wise decreasing H₂ concentration from 4% to 0.05%. For the humidity test, the relative humidity was adjusted by regulating the flow rate ratio of dry air and wet air (bubbling through DI water). The sensor was exposed to H₂ concentrations from 4% to 0.05% at the humidity level of 0%, 25%, 50%, 75% and 98% at room temperature.
Fig. S10.

**Interference/cross-sensitivity tests.** Thirty-six interference gases were tested. Their concentrations were set at 4% with only a few exceptions, including 0.4 ppm for H$_2$S, 4 ppm for NO$_2$, 4 ppm for SO$_2$, and 40 ppm for ethylene. The first panel illustrates the test protocol using CO as an example. Specifically, a J-type thermocouple coated with 1 mg Pt NP assembly was first exposed to three pulses of 4% CO in air to test whether the sensor responds to CO at room temperature, then three pulses of 4% CO but in the presence of 4% H$_2$ to access the cross-sensitivity, finally three pulses of 4% H$_2$ to test if there is irreversible poisoning.
Fig. S11.
Long-term stability test. In each cycle, the Pt NP assembly sensor was exposed to H₂ concentrations from 4% to 0.05% at room temperature. 10 cycles were conducted per day for one month to complete 288 cycles with a total testing time of 281 h.
**Fig. S12.**

**Universal applicability.** Photographs of catalytic H₂ sensors prepared from (A) liquid-in-glass thermometer; (B) J-type thermocouple/multimeter(Tekpower, Part number: TP4000ZC); (C) K-type thermocouple/multimeter; (D) pocket digital thermometer; (E) cooking thermometer; (F) thermistor (inside the A9 rectangle, dimension: ~1 mm × 2 mm). The thermistor in a circuit playground (Adafruit, Product Number: 2769) was connected to a PC by a CircuitPython Program for recording the temperature. For all experiments, the thermometer was loaded with 1 mg Pt NP assembly and exposed to 1% H₂ in air at room temperature. (G) The responses of the above six catalytic H₂ sensors at H₂ concentrations from 0.05% to 4% at room temperature. 1 mg Pt NP assembly costs less than $1, and the liquid-in-glass thermometer is ~$3 (Newark.com, #13AJ1664, $2.38 each), making the total cost of a sensor < $5 per unit.
**Fig. S13.**

**H₂ leak detection demonstration using a drone sensing platform.** 1 mg Pt NP assembly was deposited on the tip of a K-type thermocouple connected to a circuit playground (Adafruit, Product Number: 2769) with a thermocouple amplifier (Adafruit, Product Number: MAX31855) on a commercial drone (DJI Mini). The circuit playground was wirelessly connected to a smartphone by Bluetooth to report the temperature in real-time. H₂ gas was released to the hood via a tube to simulate a H₂ leakage site. Photographs of (A) the drone H₂ sensing platform, (B) the drone above the H₂ leakage site, and (C) sensor temperature readout during the test.
Fig. S14.

X-ray absorption spectroscopy results. (A) $k$-space $k^3$-weighted Pt L3-edge extended X-ray absorption fine structure (EXAFS) and (B) Fourier-transformed EXAFS data (circles) and theoretical fits (lines) of Pt foil, Pt black, Pt NPs, Pt NP assembly. (C) Coordination numbers (CN), Debye-Waller factors ($\sigma^2$), and inter-atomic distances ($R$) were obtained from the data fitting.

|          | CN | $\sigma^2$ (10$^{-3}$ Å$^2$) | $R$ (Å)  |
|----------|----|-----------------------------|---------|
| Pt-foil  | 12 | 5.3 ±0.1                    | 2.76±0.02|
| Pt-black | 12 | 9.5 ±0.1                    | 2.78±0.02|
| Pt-gel   | 12 | 10 ±0.1                     | 2.78±0.02|
| Pt-solution | 12 | 8.2 ±0.1                    | 2.77±0.02|
**Fig. S15.**

**High-resolution x-ray diffraction (XRD) spectroscopy results.** The high-resolution XRD spectra of (A) Pt NPs, (B) Pt NP assembly, and (C) Pt black were fitted using Psdvoigt 1 function in OriginPro Software into eight peaks corresponding to eight planes of (111), (200), (220), (311), (222), (400), (331), and (420). The fitted peak widths at half maximum for the three samples were summarized in (D).
Fig. S16.
Statistics of $d$-spacings obtained from the HRTEM images with 0.020 nm pixel size. Distributions of $d$-spacings for both $\{111\}$ and $\{200\}$ after analyzing HRTEM images having a pixel size of 0.020 nm are consistent with the results obtained by analyzing HRTEM images having a pixel size of 0.0149 nm (Fig. 3G). Pt NP assembly has a similar average $d$-spacing value as Pt NPs, but a larger standard deviation than Pt NPs (for $\{111\}$, standard deviation: 0.028 vs 0.021 nm; for $\{200\}$, standard deviation: 0.026 vs 0.021 nm).
Fig. S17.

**Schematics of constructing Pt $\Sigma 3$ [110] (111) GB model from two NPs.**

(A) Pt NP, modeled as a face-centered cubic (FCC) cuboctahedron, has 6 (100) facets and 8 (111) facets. The black and red lines label the (100) and (111) facets of the 2D projection of the Pt NP, respectively. (B) The two purple facets of two NPs attach after rotation by 54.735° to generate the GB model. (C) Pt $\Sigma 3$ [110] (111) GB labeled by a purple line.
Fig. S18.
Calculated strain distribution in Pt$_{783}$ $\Sigma$3 [110] (111) GB with respect to NP$_{405}$ (111) facet.
Fig. S19.
The overall reaction energy profile of hydrogen oxidation on a Pt (111) slab. (A) Associative pathway. (B) Dissociative pathway.
Fig. S20.
The overall reaction energy profile of hydrogen oxidation on the (111) facet of a Pt_{201} NP. (A) Associative pathway. (B) Dissociative pathway.
Fig. S21.
The overall reaction energy profile of hydrogen oxidation at the Pt$_{383}$ Σ3 [110] (111) GB. (A) Associative pathway. (B) Dissociative pathway.
Fig. S22.
Illustration of adsorption sites near a Pt$_{38}$ $\Sigma 3 [110]$ (111) GB. The yellow and cyan balls are the Pt atoms of NP (111) facets and GB region that favor binding with H and O, respectively.
Table S1.
The calculated reaction energy ($\Delta E$) and activation energy barrier ($E_a$) in associative pathway.

| Elementary steps          | Pt (111) slab | Pt NP | Pt GB |
|---------------------------|---------------|-------|-------|
|                           | 2.728 Å       | 2.770 Å | 2.812 Å | 2.854 Å | 2.717 Å | 2.764 Å |
| **Reaction energy / eV**  |               |       |       |       |       |       |
| $1/2 \text{H}_2(\text{g}) + * \rightleftharpoons \text{H}^*$ | -0.42 | -0.43 | -0.47 | -0.51 | -0.54 | -0.37 |
| $\text{O}_2(\text{g}) + * \rightleftharpoons \text{O}_2^*$ | -0.45 | -0.53 | -0.64 | -0.73 | -0.67 | -0.44 |
| $\text{O}_2^* + \text{H}^* \rightleftharpoons \text{OOH}^* + *$ | -0.20 | -0.13 | -0.02 | 0.04  | 0.01  | -0.32 |
| $\text{OOH}^* + \text{H}^* \rightleftharpoons 2\text{OH}^*$ | -1.61 | -1.62 | -1.66 | -1.77 | -1.72 | -1.47 |
| $\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^* + *$ | -0.72 | -0.70 | -0.62 | -0.51 | -0.49 | -0.82 |
| $\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O}(\text{g}) + *$ | -0.08 | -0.06 | -0.04 | -0.01 | 0.002 | -0.10 |
| **Activation barrier / eV** |               |       |       |       |       |       |
| $\text{O}_2^* + \text{H}^* \rightleftharpoons \text{OOH}^* + *$ | 0.38  | 0.40  | 0.41  | 0.42  | 0.40  | 0.33  |
Table S2.
The calculated reaction energy ($\Delta E$) and activation energy barrier ($E_a$) in dissociative pathway.

| Elementary steps | Pt (111) slab | Pt NP | Pt GB |
|------------------|---------------|-------|-------|
|                  | 2.728 Å       | 2.770 Å | 2.812 Å | 2.854 Å | 2.717 Å | 2.764 Å |
| **Reaction energy / eV** |               |       |       |       |       |       |
| $1/2 \text{H}_2(g) + * \rightleftharpoons \text{H}^*$ | -0.42 | -0.43 | -0.47 | -0.51 | -0.54 | -0.37 |
| $\text{O}_2(g) + * \rightleftharpoons \text{O}_2^*$ | -0.45 | -0.53 | -0.64 | -0.73 | -0.67 | -0.44 |
| $\text{O}_2^* + * \rightleftharpoons 2\text{O}^*$ | -1.20 | -1.43 | -1.63 | -1.81 | -1.56 | -1.00 |
| $\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^* + *$ | -0.30 | -0.16 | -0.03 | 0.04 | -0.08 | -0.40 |
| $\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^* + *$ | -0.72 | -0.70 | -0.62 | -0.51 | -0.49 | -0.82 |
| $\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O}(g) + *$ | -0.08 | -0.06 | -0.04 | -0.01 | 0.002 | -0.10 |
| **Activation barrier / eV** |               |       |       |       |       |       |
| $\text{O}_2^* + * \rightleftharpoons 2\text{O}^*$ | 0.72 | 0.68 | 0.63 | 0.54 | 0.57 | 0.008 |
| $\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^* + *$ | 0.75 | 0.85 | 0.91 | 0.97 | 1.02 | 0.60 |
| Micro-kinetic model parameters | value   |
|-------------------------------|---------|
| $p_{H_2}$                    | 0.04 bar|
| $p_{O_2}$                    | 0.21 bar|
| $p_{H_2O}$                   | 0.035 bar|
| $T$                          | 300K    |
Table S4.
Entropy and ZPE corrections to gas molecules and adsorbed species. The values are taken from Refs (17, 18)

| Species   | TS  | ZPE  |
|-----------|-----|------|
| H\(_2\)   | 0.41| 0.27 |
| O\(_2\)   | 0.64| 0.10 |
| H\(_2\)O  | 0.67| 0.56 |
| H\(^+\)   | 0   | 0.17 |
| O\(_2\)\(^-\) | 0  | 0.15 |
| OOH\(^+\) | 0   | 0.39 |
| OH\(^+\)  | 0   | 0.30 |
| H\(_2\)O\(^+\) | 0  | 0.62 |
| O\(^+\)   | 0   | 0.07 |
**Movie S1.**  
Demonstration of H$_2$ leak detection using a drone sensing platform.

**Movie S2.**  
Demonstration of detection of 2% H$_2$ in air.
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