SUPPORTING INFORMATION

Electrocatalysis Under Cover: Enhanced Hydrogen Evolution via Defective Graphene Covered Pt(111)

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7. References
1. Impurities in Chemicals and Back-of-Envelope Calculations

1.1. Chemicals used and their impurities

Table S01: Purity and impurities listed for liquids used to wash glassware

<table>
<thead>
<tr>
<th>Chemical Vendor and Item ID</th>
<th>Impurities listed by manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra High Purity Water Millipore</td>
<td>&lt; 5 ppb total organic content (TOC) 18.2 MΩ·cm at 25 °C</td>
</tr>
<tr>
<td>Potassium permanganate (KMnO₄) ≥ 99.0 % Sigma Aldrich 223468-500G</td>
<td>Chloride, Chlorate (as Cl⁻): ≤ 0.005 % Sulfate (SO₄²⁻): ≤ 0.02 %</td>
</tr>
<tr>
<td>Sulfuric Acid (H₂SO₄) 95.0 – 97.0 % Sigma Aldrich 30743-1L-M</td>
<td>Chloride (Cl⁻): ≤ 0.1 mg/kg (ppm) Nitrate (NO₃⁻): ≤ 0.2 mg/kg (ppm) Phosphate (PO₄³⁻): ≤ 0.00005% (0.5 ppm)</td>
</tr>
<tr>
<td>Hydrogen Peroxide (H₂O₂) 35% Merck KGaA 108600</td>
<td>Sulfuric Acid (H₂SO₄): ≤ 0.025 % Pb heavy metal: ≤ 0.0002 % Chloride (Cl⁻): ≤ 0.005 % Residual solvents (ICH Q3C): excluded from production process Non volatile matter: ≤ 0.10 % Residue on ignition: ≤ 0.05 % Preservatives: Na₂H₂P₂O₇: 0.015% H₃PO₄: 0.01% NH₄NO₃: 0.006% Sn: 0.001%</td>
</tr>
</tbody>
</table>

Table S02: Purity and impurities listed for liquids for electrolyte

<table>
<thead>
<tr>
<th>Chemical Vendor and Item ID</th>
<th>Impurities listed by manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra High Purity Water Millipore</td>
<td>&lt; 5 ppb total organic content (TOC) 18.2 MΩ·cm at 25 °C</td>
</tr>
<tr>
<td>Sulfuric Acid (H₂SO₄) ≥ 95 % Sigma Aldrich 77329-250ML-F</td>
<td>Chloride (Cl⁻): ≤ 0.5 mg/kg (ppm) Nitrate (NO₃⁻): ≤ 0.1 mg/kg (ppm) Phosphate (PO₄³⁻): ≤ 0.5 mg/kg (ppm)</td>
</tr>
</tbody>
</table>
**Table S03:** Purity listed on cylinder and impurities for gases used to purge electrolyte and to quench Pt(111) after flame annealing. 6.0 grade gases were used for Pt(111) and G/Pt(111)#1 through #3. 5.0 grade gases were used for G/Pt(111)#4. (See Table S09 for list of G/Pt(111) electrodes synthesized and tested). No differences in the CVs and HER currents were observed between these two purities.

<table>
<thead>
<tr>
<th>Chemical Vendor and Item ID</th>
<th>Impurities listed by manufacturer</th>
</tr>
</thead>
</table>
| Argon Linde 6.0 Scientific Grade ≥ 99.9999% | N₂ ≤ 0.5 ppm  
H₂ ≤ 0.2 ppm  
O₂ ≤ 0.5 ppm  
Total hydrocarbon content (THC) ≤ 0.1 ppm  
H₂O ≤ 0.5 ppm  
CO₂ ≤ 0.1 ppm  
CO ≤ 0.1 ppm |
| Argon Linde 5.0 grade ≥ 99.999% | N₂ ≤ 5 ppm  
O₂ ≤ 2 ppm  
Total hydrocarbon content (THC) ≤ 0.2 ppm  
H₂O ≤ 3 ppm |
| Hydrogen Linde 6.0 High Purity ≥ 99.9999% | N₂ ≤ 1 ppm  
O₂ ≤ 0.7 ppm  
Total hydrocarbon content (THC) ≤ 0.1 ppm  
H₂O ≤ 1 ppm  
CO ≤ 0.1 ppm  
CO₂ ≤ 0.1 ppm |
| Hydrogen Linde 5.0 Detector Grade ≥ 99.999% | N₂ ≤ 3 ppm  
Total hydrocarbon content (THC) ≤ 0.5 ppm  
O₂ ≤ 2 ppm  
H₂O ≤ 5 ppm |
**Table S04:** Composition of butane fuel mixture used for annealing Pt(111) and HNO₃ used for etching impurities off Pt(111).

<table>
<thead>
<tr>
<th>Chemical Vendor and Item ID</th>
<th>Impurities listed by manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>FlameClassics Universal Gas Lighter Refill</td>
<td>Propane 40.0% Butane 30.0% Isobutane 30.0% 1,3-Butadiene &lt; 0.1%</td>
</tr>
<tr>
<td>Nitric Acid (HNO₃) ≥ 65% Suprapur® Merck Millipore 1004411000</td>
<td>Residue on ignition (as sulfate) ≤ 2 ppm Cl ≤ 50 ppb PO₄ ≤ 10 ppb SO₄ ≤ 200 ppb Al, Ni ≤ 5.0 ppb Ca, Fe, K, Pb, Zn ≤ 2.0 ppb Cr, Hg, Mg, Ti, Zr ≤ 1.0 ppb Ag, As, Ba, Be, Bi, Cd, Co, Cu, In, Li, Mn, Mo, Pt, Sb, Sn, Sr, Tl, V ≤ 0.5 ppb Au, Ga, Ge ≤ 0.1 ppb</td>
</tr>
</tbody>
</table>

**Table S05:** Composition of gases used for graphene growth on Pt(111) via chemical vapor deposition

<table>
<thead>
<tr>
<th>Chemical Vendor and Item ID</th>
<th>Impurities listed by manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon Linde 5.0 grade ≥ 99.999%</td>
<td>N₂ ≤ 5 ppm O₂ ≤ 2 ppm Total hydrocarbon content (THC) ≤ 0.2 ppm H₂O ≤ 3 ppm</td>
</tr>
<tr>
<td>Hydrogen Linde 5.0 Detector Grade ≥ 99.999%</td>
<td>N₂ ≤ 3 ppm Total hydrocarbon content (THC) ≤ 0.5 ppm O₂ ≤ 2 ppm H₂O ≤ 5 ppm</td>
</tr>
<tr>
<td>Ethylene Linde 4.5 Grade ≥ 99.995%</td>
<td>N₂ ≤ 5 ppm O₂ ≤ 2 ppm H₂O ≤ 5 ppm CO₂ ≤ 5 ppm Others ≤ 40 ppm</td>
</tr>
</tbody>
</table>
1.2. Solubility of H₂ in aqueous H₂SO₄ and time for saturation

Solubilities of H₂ in H₂SO₄ solutions

Solubility in 0.5 M H₂SO₄:

\[
\left(0.59 \frac{mol}{L}\right) \times (0.1 \, L) = 0.059 \, mol \, H₂
\]

Solubility in water (0 M H₂SO₄):

\[
\left(0.63 \frac{mol}{L}\right) \times (0.1 \, L) = 0.063 \, mol \, H₂
\]

Time required to saturate electrolyte with H₂

Flow rate of H₂:

\[
\left(100 \ to \ 500 \ \frac{mL}{min}\right) \times \left(\frac{1 \, mol}{22.4 \, L}\right) \times \left(\frac{1 \, L}{1000 \, mL}\right) = 0.0045 \ to \ 0.022 \, mol \, H₂ \, min^{-1}
\]

Assuming no bypassing during bubbling, it will take 2.6 to 14 minutes to saturate 100 mL of electrolyte (molarities between 0 and 0.5 M H₂SO₄) with pure H₂.

Time required to saturate electrolyte with H₂ produced from electrolysis

The maximum observed HER current is \(~10 \, mA \, cm^{-2}\), so we use this as a conservative H₂ production rate in our calculations.

\[
\left(10 \ \frac{mA}{cm^2}\right) \times (0.385 \, cm^2) \times \left(\frac{6.2 \cdot 10^{18} \ \text{electrons}}{second} \right) \times \left(\frac{1 \, A}{1000 \, mA}\right) \times \left(\frac{1 \, molecule \, H₂}{2 \, electrons}\right) \times \left(\frac{1 \, mol}{6.02 \cdot 10^{23} \, molecule \, H₂}\right)
\]

\[
(80 \, minutes) \times \left(\frac{60 \, seconds}{minute}\right) = 0.000095 \, mol \, H₂
\]

Throughout the experiment, the amount of H₂ produced is less than 1/660 the saturation limit of H₂ in H₂SO₄. It will take at least 34 days to fully saturate the electrolyte with H₂.
1.3. Tunneling, diffusion, and HER rates: order of magnitude comparisons

He tunneling rates:\(^5\):

\[
\left( \frac{10^5 \text{ to } 10^6 \text{ atoms He}}{s} \right) \left( \frac{1}{2\pi \left( \frac{4}{2} \right)^2 \mu m^2} \right) \left( \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \right) \left( \frac{10^4 \mu m}{cm} \right)^2 \\
= 6.6 \times 10^{-13} \text{ to } 6.6 \times 10^{-12} \frac{\text{mol He}}{s \text{ cm}^2}
\]

Ar and Air tunneling rates:\(^6\):

\[
\left( \frac{10^3 \text{ atoms He}}{s} \right) \left( \frac{1}{2\pi \left( \frac{4}{2} \right)^2 \mu m^2} \right) \left( \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \right) \left( \frac{10^4 \mu m}{cm} \right)^2 = 6.6 \times 10^{-15} \frac{\text{mol}}{s \text{ cm}^2}
\]

H\(^+\) tunneling rate:\(^7\):

\[
(0.4 \frac{mA}{cm^2}) \left( \frac{6.2 \times 10^{18} \text{protons}}{second} \right) \left( \frac{1 A}{10^3 mA} \right) \left( \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ proton}} \right) = 4.1 \times 10^{-8} \frac{\text{mol}}{s \text{ cm}^2}
\]

H\(_2\) diffusion rate:\(^8\):

\[
J = -D \frac{\Delta C}{\Delta x} = - \left( 4.5 \times 10^{-5} \frac{cm^2}{s} \right) \left( \frac{0.09 \frac{g H_2}{L}}{0.5 \text{ nm}} \right) \left( \frac{1 \text{ mol}}{1.00789 \text{ g}} \right) \left( 10^7 \text{ nm} \right) \left( 1 \frac{L}{10^3 \text{ cm}^3} \right)
\]

\[
* f = 0.45 \frac{mol}{s \text{ cm}^2} = 0.45 \times 0.01 \frac{mol}{s \text{ cm}^2} = 4.5 \times 10^{-5} \frac{mol}{s \text{ cm}^2}
\]

where \(f\) = areal fraction of defects (holes/grain boundaries) in the graphene

Production rate of H\(_2\):

The maximum-observed HER current is \(\sim 10\ mA \ cm^2\), so we will use this as a conservative rate.

\[
(10 \frac{mA}{cm^2}) \left( \frac{6.2 \times 10^{18} \text{electrons}}{second} \right) \left( \frac{1 A}{10^3 mA} \right) \left( \frac{1 \text{ molecule } H_2}{2 \text{ electrons}} \right) \left( \frac{1}{6.022 \times 10^{23} \text{ molecule } H_2} \right)
\]

\[
= 5.1 \times 10^{-8} \frac{\text{mol}}{s \text{ cm}^2}
\]
Table S06: Order-of-magnitude transport rates of He, Ar, air, H\textsubscript{2}, and H\textsuperscript{+} through graphene rounded to the next highest magnitude.

<table>
<thead>
<tr>
<th>Transport Phenomenon</th>
<th>Rate / mol s\textsuperscript{-1} cm\textsuperscript{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>He tunneling \textsuperscript{5}</td>
<td>10\textsuperscript{-11}</td>
</tr>
<tr>
<td>Ar and air tunneling \textsuperscript{6}</td>
<td>10\textsuperscript{-14}</td>
</tr>
<tr>
<td>H\textsuperscript{+} tunneling \textsuperscript{7}</td>
<td>10\textsuperscript{-7}</td>
</tr>
<tr>
<td>H\textsubscript{2} diffusion \textsuperscript{8}</td>
<td>10\textsuperscript{-4}</td>
</tr>
<tr>
<td>H\textsubscript{2} evolution (this work)</td>
<td>10\textsuperscript{-7}</td>
</tr>
</tbody>
</table>
2. Benchmarking with Literature and Validation Tests

2.1. Characterization of Pt(111) using Cyclic Voltammetry (CV) and Cyclic Amperometry

Figure S01: Steady state currents for kinetic analysis were collected by holding overpotentials between 0.0 and -0.1 V_RHE for 4 minutes to allow the current to stabilize. Repeats and semi-randomized overpotentials were used to avoid and shine light on potential systematic drifts in data collection.

2.2. Benchmarking CVs of Pt(111) in H₂SO₄ with literature

Figure S02 plots cyclic voltammograms (cycled at 50 mV s⁻¹ between 0.1 to either 0.8 or 1.0 V_RHE) in H₂SO₄ at concentrations between 0.005 and 0.5 M H₂SO₄. We observe a systematic shift in the sharp sulfate peak to higher overpotentials (Figure S03) and a concurrent decrease in the sulfate peak intensity (Figure S04) with increasing H₂SO₄ concentration. The sulfate peak overpotentials and intensities of Pt(111) in H₂SO₄ from the literature included a benchmark 9-17. For all literature comparisons, DataThief III was used to extract data from graphs 18,19.

Figure S02: Cyclic voltammograms of Pt(111) between 0.005 and 0.5 M H₂SO₄.
Figure S03: Overpotential of the sharp $\text{SO}_4^{2-}$ peak from Pt(111) cyclic voltammograms plotted against $\text{H}_2\text{SO}_4$ concentration. Values extracted from literature are presented as colored diamonds.

Figure S04: Maximum current density of the sharp $\text{SO}_4^{2-}$ peak from Pt(111) cyclic voltammograms plotted against $\text{H}_2\text{SO}_4$ concentration. Values extracted from literature are presented as colored diamonds.
2.3. Benchmarking HER currents of Pt(111) in H$_2$SO$_4$ with literature

For all literature comparisons, DataThief III was used to extract data from graphs$^{18,19}$.

**Figure S05:** Currents measured for Pt(111) in inert gas purged 0.5 M H$_2$SO$_4$ at 293 K between potentials of 0 and -0.08$\text{RHE}$. Kita et al. used N$_2$ to purge the electrolyte$^{20}$. Gómez et al. and this work used Ar to purge the electrolyte$^{21}$. The ramp rate is 10 mV s$^{-1}$. All currents are normalized to the areal surface are of the Pt(111) electrode. All currents measured are within 20% of each other.

**Figure S06:** Currents measured for Pt(111) in H$_2$ purged 0.5 M H$_2$SO$_4$ at 293 K between potentials of 0 and -0.08$\text{RHE}$ at temperatures of 274 and 303 K (22) and 293 K (this work). An Arrhenius plot of the currents at -0.025 V$_\text{RHE}$ (shown in inset) displays an apparent activation energy of 10 ± 12 kJ mol$^{-1}$, within error of the apparent activation energy of 18 kJ mol$^{-1}$ reported by Marković et al.$^{22}$. 

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Figure S07: Relation between the overpotential and the log of the current for Pt(111) in H$_2$SO$_4$ with molarities between 0.005 and 0.5 M. No dependence with the rotation rate is observed between the measured current and the overpotential (0 to -0.1 V$_{RHE}$).

Figure S08: Relation between the measured current and the rotation rate of the Pt(111) disk at -0.08V$_{RHE}$. No dependence with the rotation rate is observed between the measured current and the overpotential (0 to -0.1 V$_{RHE}$).

Figure S09: Relation between the % increase of the measured current and the rotation rate of the Pt(111) disk at -0.08V$_{RHE}$. A 95% confidence error of ~20% was observed for all molarities for Pt(111) in H$_2$SO$_4$. 
3. Electrochemical Measurements

3.1. Measuring molarities with the dilution equation and a pH meter

H$_2$SO$_4$ molarities were measured using two different methods: dilution equation (Equation S01 and S02) and pH meter (Equations S03). We observed parity between molarities measured except at 0.5 M H$_2$SO$_4$ (pH 0.3) likely because extrapolation from the pH meter calibration (pH 2 to 7) was required to calculate the molarity for 0.5 M H$_2$SO$_4$. Because of this, when graphing $[\text{H}^+]$ order plots, molarities measured from the pH probe was used for molarities between 0.005 and 0.05 M H$_2$SO$_4$, and molarities calculated from the dilution equation was used for 0.5 M H$_2$SO$_4$.

Dilution Equation:

\[
C_1 V_1 = C_2 (V_1 + V_2) \quad \text{(Equation S01)}
\]

\[
C_2 = \frac{C_1 V_1}{V_1 + V_2} \quad \text{(Equation S02)}
\]

Where $C_1$ and $V_1$ are the concentration and volume of the undiluted H$_2$SO$_4$ solution needing to be diluted, $V_2$ is the volume of water added. $C_2$ is the final diluted concentration.

pH Calibration Equation:

\[
\text{pH} = mU + b \quad \text{(Equation S03)}
\]

Where $m$ and $b$ are the slope and $y$-intercept of the pH probe calibration, $U$ is the potential difference (typically in mV) measured by the pH probe.

Figure S10: Calibration plots used to convert the potential difference measured by the pH probe to the electrolyte pH at the end of electrochemical measurements. A calibration was created manually before and after each batch of samples to ensure no drift in the pH probe. The calibration did not shift significantly throughout each batch of measurements and throughout the time all measurements in this study were performed.
3.2. Correcting for internal resistance

The internal resistance (iR) through wires and electrolyte between the working and counter electrode was collected after every electrochemical experiment. Figure S12 plots the measured iR against the H₂SO₄ concentration. We observe significant increases in the iR at concentrations below 0.1 M H₂SO₄. Equation S04 is used to correct overpotentials where E is the electrode overpotential corrected for iR, E₀ is the measured electrode overpotential, R is the resistance and I is the current. We observe that the iR can induce up to a 0.04 V_RHE shift at 0.005 M H₂SO₄ and -0.08 V_RHE.

\[ E = E_0 - IR \] (Equation S04)

Figure S12: The measured internal resistance plotted versus the H₂SO₄ concentration for a typical electrochemical cell setup. It should be noted that the internal resistance is also dependent on a number of factors assumed to be constant, such as the geometry of the electrodes and distance between the electrodes. Care was taken to ensure that a near-identical electrochemical set up was used and care was taken to only change the electrolyte molarity between runs.
3.3. Overpotential window where kinetics are dominated by HER

Intrinsic Tafel behavior reflects irreversible kinetics, which only occurs at high overpotentials for reversible reactions, such as HER (Equation S05)\(^2\). The total steady state current density due to a reversible chemical reaction is expressed as the sum of an oxidative and reductive current (Equation S06). Since both oxidative and reductive currents obey a Tafel expression, the ratio of their rates can be used to calculate the overpotential window where kinetics are dominated by reduction (Equation S07). Assuming that reduction dominates when the ratio of the oxidation and reduction currents is less than 0.01, we calculate that HER dominates at overpotentials lower than -0.06 V\(_{\text{RHE}}\) (Equation S08).

\[ 2H^+ + 2e^- \xrightarrow{\text{reduction}} H_2 \]  \hspace{1cm} \text{(Equation S05)}

\[ i_{\text{total}} = i_{\text{oxidation}} + i_{\text{reduction}} \]  \hspace{1cm} \text{(Equation S06)}

\[ \frac{i_{\text{reduction}}}{i_{\text{oxidation}}} = \frac{i_{\text{HER}}}{i_{\text{HOR}}} = e^{\frac{2F\eta}{RT}} \]  \hspace{1cm} \text{(Equation S07)}

\[ \frac{i_{\text{HOR}}}{i_{\text{HER}}} = e^{\frac{2F\eta}{RT}} < 0.01 \text{ when } \eta < -0.06 \text{ V}_{\text{RHE}} \]  \hspace{1cm} \text{(Equation S08)}

3.4. Normal Hydrogen Electrode (NHE) reference calculations

Since the reversible hydrogen electrode (RHE) is based on the half-cell reaction \(2H^+ + 2e^- \rightarrow H_2\), and the reaction is affected by the pH (H\(^+\) concentration), the RHE systematically shifts with the pH. Because the normal hydrogen electrode (NHE) reference does not shift with the pH, we should ideally correct our measured overpotentials to be in line with the NHE reference for kinetic measurements. Equation S10 and Table S07 demonstrate that the RHE overpotential can shifts by as much as 0.12 V in the pH range studied.

\[ E = E_o - \frac{RT}{nF} \ln[H^+] \]  \hspace{1cm} \text{(Equation S09)}

\[ E_{\text{RHE}} = 0.0591 \cdot pH \text{ at } 25^\circ\text{C} \text{ and } 1 \text{ atm} \]  \hspace{1cm} \text{(Equation S10)}

Figure S13 demonstrates how Tafel plot data collected on Pt(111) in H\(_2\)SO\(_4\) (0.005, 0.05, and 0.5 M) transform upon converting the reference overpotential from a reversible hydrogen electrode (RHE) scale to a normal hydrogen electrode (NHE) scale. We observe that a decrease in concentration shifts the Tafel plots to lower overpotentials on the NHE scale. This makes it difficult, across the 2 order-of-magnitude concentration range, to properly collect and compare intrinsic currents free of mass-transfer effects (at low overpotentials < ~ -0.08 V\(_{\text{RHE}}\)) or low HER efficiencies (at higher overpotentials > ~ -0.06 V\(_{\text{RHE}}\)) without the need for extrapolation. \([H^+]\) orders of HER on Pt(111) in Ar-purged (Figure S14) and H\(_2\)-purged (Figure S15) H\(_2\)SO\(_4\) increase from ~0.6 on the RHE scale to 1.2 on the NHE scale. This might explain why reaction orders,
though predicted to be 1 from the rate laws, often result in fractional orders of ~0.5.

**Table S07:** How the RHE and NHE references change with molarities between 0.005 and 0.5 M \( \text{H}_2\text{SO}_4 \)

<table>
<thead>
<tr>
<th>Molarity / M</th>
<th>pH</th>
<th>( E/V_{\text{RHE}} )</th>
<th>( E/V_{\text{NHE}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>2.3</td>
<td>0.14</td>
<td>0.00</td>
</tr>
<tr>
<td>0.02</td>
<td>1.7</td>
<td>0.10</td>
<td>0.00</td>
</tr>
<tr>
<td>0.05</td>
<td>1.3</td>
<td>0.08</td>
<td>0.00</td>
</tr>
<tr>
<td>0.10</td>
<td>1.0</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td>0.33</td>
<td>0.48</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>0.50</td>
<td>0.30</td>
<td>0.02</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Figure S13:** Tafel plots of HER currents on Pt(111) in Ar-purged (hollow circles) and H\(_2\)-purged (solid circles) \( \text{H}_2\text{SO}_4 \) electrolyte. Raw currents (left graph) and currents corrected for internal resistance and NHE (right) are displayed for side-by-side comparison.
Figure S14: \([\text{H}^+]\) order plots in Ar-purged \(\text{H}_2\text{SO}_4\) electrolyte on Pt(111). Left: iR-corrected currents only. Right: iR-corrected and NHE-corrected currents. The circled currents were measured in low concentration \(\text{H}_2\text{SO}_4\) (0.005 and 0.02 M) and were heavily extrapolated after fitting the data to an exponential function.

Figure S15: \([\text{H}^+]\) order plots in \(\text{H}_2\)-purged \(\text{H}_2\text{SO}_4\) electrolyte on Pt(111). Left: iR-corrected currents only. Right: iR-corrected and NHE-corrected currents. The circled currents were measured in low concentration \(\text{H}_2\text{SO}_4\) (0.005 and 0.02 M) and were heavily extrapolated after fitting the Tafel data to an exponential function. Excluded data points in the graph on the right were so noisy that errors after extrapolation were > 100%.
3.5. HER Tafel Plots and Tafel Slope versus Overpotential

**Figure S16:** HER Tafel plots in H$_2$-saturated H$_2$SO$_4$ on (A) Pt(111), (B) as-prepared G/Pt(111), and (C) EC-treated G/Pt(111) collected at steady-state (chronoamperometry) after HER reaction time of > 10 h at overpotentials between -0.10 and 0.00 V$_{RHE}$. (D) The Tafel slope as a function of the overpotential for Pt(111) in 0.005, 0.05, and 0.5 M H$_2$SO$_4$ and 0.1 M HClO$_4$. HER currents collected in HClO$_4$ is the first cathodic (negative sweeping) scan at 10 mV s$^{-1}$.

3.6. Volmer-Heyrovský and Volmer-Tafel rate laws

Elementary steps involved in transforming H$^+$ to H$_2$ involve the three steps below. These steps involve adsorption and electron transfer with a surface site (Volmer step), then reaction with a proton in solution (Heyrovsky step) or reaction with an adsorbed surface H (Tafel step) to form H$_2$. Table S08 lists predicted Tafel slopes and [H$^+$] orders from rate laws derived from elementary steps.
Volmer step: $H_3O^+ + e^- + * \rightleftharpoons H* + H_2O$

Heyrovsky step: $H* + H_3O^+ + e^- \rightleftharpoons H_2 + H_2O + *$

Tafel step: $2H* \rightleftharpoons H_2 + 2*$

**Table S08:** Summary of predicted Tafel slopes and $[H^+]$ orders from rate law derivations with different coverages and rate limiting steps.

<table>
<thead>
<tr>
<th>Rate Limiting Step</th>
<th>Coverage</th>
<th>Tafel slope / mV dec$^{-1}$</th>
<th>$[H^+]$ order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volmer</td>
<td>$\theta = 0$</td>
<td>120</td>
<td>1</td>
</tr>
<tr>
<td>Heyrovský</td>
<td>$\theta = 1$</td>
<td>120</td>
<td>1</td>
</tr>
<tr>
<td>Tafel</td>
<td>$\theta = 1$</td>
<td>$\infty$</td>
<td>0</td>
</tr>
</tbody>
</table>

3.7. **Table of G/Pt(111) electrodes synthesized and tested in this work**

**Table S09:** List of electrodes synthesized and tested in this work.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Diameter / mm</th>
<th>Pretreatment(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>7</td>
<td>Etched in HNO$_3$ and annealed then cooled in H$_2$/Ar</td>
</tr>
<tr>
<td>G/Pt(111)#1</td>
<td>7</td>
<td>Electrochemical cycling pretreatment</td>
</tr>
<tr>
<td>G/Pt(111)#2_1</td>
<td>7</td>
<td>Electrochemical cycling pretreatment</td>
</tr>
<tr>
<td>G/Pt(111)#2_2</td>
<td>7</td>
<td>Only Electrochemical cycling</td>
</tr>
<tr>
<td>G/Pt(111)#3_1</td>
<td>6</td>
<td>No electrochemical cycling pretreatment</td>
</tr>
<tr>
<td>G/Pt(111)#3_2</td>
<td>10</td>
<td>No electrochemical cycling pretreatment</td>
</tr>
<tr>
<td>G/Pt(111)#3_3</td>
<td>10</td>
<td>No electrochemical cycling pretreatment</td>
</tr>
<tr>
<td>G/Pt(111)#4</td>
<td>7</td>
<td>No electrochemical cycling pretreatment</td>
</tr>
</tbody>
</table>

3.8. **Effect of sequential EC-treatment on HER currents and CVs on G/Pt(111)**

**Table S10:** Summary of the sequential EC treatment subjected on G/Pt(111).

<table>
<thead>
<tr>
<th>Defect generation method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>sequential EC-treated G/Pt(111)</td>
<td>Alternating between: (1) 250 cycles between 0.1 to 1.2 V$_{RHE}$ at 500 mV s$^{-1}$ in 0.05 M H$_2$SO$<em>4$ and (2) 4 minutes of HER at -0.08 V$</em>{RHE}$ in 0.05 M H$_2$SO$_4$</td>
</tr>
</tbody>
</table>
Figure S17: Geometric current densities measured in 0.05 M H$_2$SO$_4$ at -0.08 V$_{	ext{RHE}}$. Solid and hollow shapes are currents collected at 0 rpm and 3000 rpm, respectively. HER currents (A) and corresponding CVs (B) as a function of cycle number. HER currents were steady state (chronoamperometry) measured at -0.08 V$_{	ext{RHE}}$ in 0.05 M H$_2$SO$_4$ on electrochemically pretreated G/Pt(111).

3.9. Integrating CVs to obtain adsorption capacities in mols per e$^-$

Cyclic voltammograms (CVs) of G/Pt(111) electrodes exhibit two regions: a H$^+$ adsorption region between 0.1 and 0.4 V$_{	ext{RHE}}$ where primarily H$^+$ adsorbs and desorbs from the electrode and a double layer region between 0.4 and 0.8 V$_{	ext{RHE}}$ where anions adsorb and desorb from the electrode. Because defects in the graphene overlayers change differently depending on the pretreatment throughout the course of HER, we can quantify the two regions using Equation S12 and plot them as a function of time (Figures S19 and S20). The slope allows us to quantify the rate at which the defects increase (Equation S13).

Equation S11 is used to calculate the total mols of electrons, where F is Faraday’s constant. The total mols of electrons is further normalized per surface Pt on the Pt(111) surface with Equation S12, where A is the geometric area of the electrode, $N_A$ is Avogadro’s Number, and $\rho_{\text{Pt}(111)}$ is the surface Pt density of Pt(111) ($1.503 \times 10^{15}$ atoms cm$^{-2}$).
Figure S18: A typical CV for G/Pt(111) electrodes. The H\textsubscript{UPD} region was quantified via integration between 0.1 and 0.4 V\textsubscript{RHE}. The anion region was quantified via integration between 0.4 and 0.8 V\textsubscript{RHE}.

\[ \text{mol}_{e^-} = \frac{1}{f} \int i \, dt \quad \text{(Equation S11)} \]

\[ f = \frac{\text{mol}_{e^-}}{\text{mol}_{Pt(111)}} = \frac{1}{N_A} \left( \frac{\int i \, dt}{P_{Pt(111)}} \right) \quad \text{(Equation S12)} \]

\[ r_{\text{defect generation}} = \frac{df_{\text{anion}}}{dt} \quad \text{(Equation S13)} \]

3.10. Changes in H\textsuperscript{+} and anion coverages with HER reaction time

Using the methodology outlined in Supp. Info. Section 3.9, H\textsuperscript{+} and anion coverages were calculated for CVs on both non-pretreated and pretreated G/Pt(111) at various HER reaction times. On non-pretreated G/Pt(111), a sudden increase in the anion coverage is observed at ~10 ± 2 hours of HER (Figure S19). No sudden increase in the anion coverage, but rather, a gradual increase is observed for pretreated G/Pt(111) with increasing HER reaction time (Figure S20).
**Figure S19:** H⁺ adsorption coverages (red) and anion adsorption coverages (blue) for the 4 non-pretreated G/Pt(111) electrodes tested. G/Pt(111)#3_2 was only tested to 4 hours HER due to unforeseen circumstances in the laboratory. The other three electrodes all exhibited sudden increases in the anion coverage ~10 hours of HER. Data is separated into 3 plots for clarity.

**Figure S20:** H⁺ adsorption coverages (red) and anion adsorption coverages (blue) for the 2 pretreated G/Pt(111) electrodes. G/Pt(111)#1 exhibited no sudden increase in anion coverages for up to 15 hours and G/Pt(111)#2 exhibited no sudden increase in anion coverages for up to 8 hours.

**Figure S21:** Zoom-in of the anion coverages with HER reaction time prior to the sudden increase in anion coverage (left). The slope of a best fit line to each of these data sets represent the rate of defect generation (right). We observe that non-pretreated G/Pt(111) exhibit lower defect generation rates than pretreated G/Pt(111) prior to the sudden increase in anion coverage. This indicates oxidative pretreatment (cycling 250 times between 0.1 and 1.2 V_{RHE} at 500 mV s⁻¹ in 0.005 M H₂SO₄) increases the rate of defect generation.

**Table S11:** Concentration at which non-pretreated G/Pt(111) exhibited a sudden increase in anion coverage after ~10 h HER.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>H₂SO₄ concentration / M</th>
</tr>
</thead>
</table>

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### 3.11. Koutecký–Levich plots for Pt(111) and G/Pt(111)

As demonstrated with the Levich Equation (Equation S14) [58,60], Koutecký–Levich plots on Pt(111) and G/Pt(111) electrodes exhibit data whose y-intercept intercepts at values greater than zero (Figure S22). This indicates that our measured HER currents not transport limited from transport of $H^+$ to or $H_2$ from G/Pt(111) under the conditions studied (in both Ar- and H$_2$-saturated 0.005 to 0.5 M H$_2$SO$_4$ at 23°C at -0.08 V$_{RHE}$). Leaist$^{29}$ demonstrated that the diffusivity of $H^+$ is higher in 0.005 M H$_2$SO$_4$ than 0.5 M H$_2$SO$_4$, indicating that it is unlikely that these differences in HER currents is due to changes in the diffusivity of $H^+$ in different electrolyte. Instead possible explanations may reside in: changes in the fraction of $H^+$, HSO$_4^-$, and SO$_4^{2-}$ species (which are heavily dependent on the molarity) and/or changes in solvation as protons are stripped of their solvation shell while travelling across the graphene interface into the slit between graphene and Pt(111).

$$\frac{1}{i_L} = \left(\frac{1}{0.620 nFAD^2v^{-1/6}c}\right) \omega^{-1/2} \quad \text{(Equation S14)}$$
**Figure S22**: Koutecký–Levich Plot for Pt(111) (grey), pretreated G/Pt(111) (red), and non-pretreated G/Pt(111) (blue) after stabilization of the currents (> 10 hours HER for G/Pt(111)) at -0.08 V_{RHE} in H_2-saturated electrolyte (0.005, 0.05, and 0.5 M H_2SO_4). Error bars are 2 times the standard deviation.

4. Error Propagation Equations for Calculating the Uncertainty

When experimental measurements and calculations involve several measurements, each with its own uncertainty, error propagation was used to calculate the uncertainty using standard propagation of error formulas. Errors of slopes were calculated using the LINEST() function in Microsoft Excel.
Table S12: The variance calculated using propagation of error formulas for experimental measurements in this study.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution Equation</td>
<td>[ \sigma_2^2 = \left( \frac{dC_2}{dC_1} \right)^2 \sigma_1^2 + \left( \frac{dC_2}{dV_1} \right)^2 \sigma_{V_1} + \left( \frac{dC_2}{dV_2} \right)^2 \sigma_{V_2} ]</td>
</tr>
<tr>
<td></td>
<td>[ \sigma_2^2 = \left( \frac{V_1}{V_1 + V_2} \right)^2 \sigma_{C_1} + \left( \frac{C_1V_2}{(V_1 + V_2)^2} \right)^2 \sigma_{V_1} ]</td>
</tr>
<tr>
<td></td>
<td>[ + \left( - \frac{C_1V_1}{(V_1 + V_2)^2} \right)^2 \sigma_{V_2} ]</td>
</tr>
<tr>
<td>pH Calibration Equation</td>
<td>[ \sigma_{pH} = \left( \frac{d(pH)}{dm} \right)^2 \sigma_m + \left( \frac{d(pH)}{dU} \right)^2 \sigma_U^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ + \left( \frac{d(pH)}{db} \right)^2 \sigma_b^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ \sigma_{pH} = U^2 \sigma_m^2 + m^2 \sigma_U^2 + 1^2 \sigma_b^2 ]</td>
</tr>
<tr>
<td>Concentration from pH calibration equation</td>
<td>[ \sigma_{[H^+]}^2 = \left( \frac{d([H^+])}{dm} \right)^2 \sigma_m^2 + \left( \frac{d([H^+])}{dU} \right)^2 \sigma_U^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ + \left( \frac{d([H^+])}{db} \right)^2 \sigma_b^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ \sigma_{[H^+]} = \left( -U \ln(10) 10^{-(mU+b)} \right)^2 \sigma_m^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ + \left( -m \ln(10) 10^{-(mU+b)} \right)^2 \sigma_U^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ + \left( -\ln(10) 10^{-(mU+b)} \right)^2 \sigma_b^2 ]</td>
</tr>
<tr>
<td>iR Corrected Overpotentials</td>
<td>[ \sigma_{RHE}^2 = \left( \frac{\partial V_{RHE}}{\partial V_o} \right)^2 \sigma_{V_o}^2 + \left( \frac{\partial V_{RHE}}{\partial i} \right)^2 \sigma_{i}^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ + \left( \frac{\partial V_{RHE}}{\partial R} \right)^2 \sigma_{R}^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ \sigma_{RHE}^2 = \sigma_{V_o}^2 + R^2 \sigma_i^2 + i^2 \sigma_{R}^2 ]</td>
</tr>
<tr>
<td>iR and NHE Corrected Overpotentials</td>
<td>[ \sigma_{NHE}^2 = \left( \frac{\partial V_{NHE}}{\partial V_o} \right)^2 \sigma_{V_o}^2 + \left( \frac{\partial V_{NHE}}{\partial i} \right)^2 \sigma_{i}^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ + \left( \frac{\partial V_{NHE}}{\partial R} \right)^2 \sigma_{R}^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ + \left( \frac{\partial V_{NHE}}{\partial [H^+]} \right)^2 \sigma_{[H^+]}^2 ]</td>
</tr>
</tbody>
</table>
$$\sigma_{v, NHE}^2 = \sigma_{v_0}^2 - R\sigma_i^2 - i\sigma_R^2 + 0.0591[H^+]^{-1}\sigma_{[H^+]}^2$$

### Koutecký-Levich Plot y-axis

\( y = i^{-1} \)

\[
\sigma_y^2 = \left(\frac{\partial y}{\partial i}\right)^2 \sigma_i^2 \\
\sigma_y^2 = i^{-4} \sigma_i^2
\]

### Koutecký-Levich Plot x-axis

\( x = \omega^{-1/2} \)

\[
\sigma_x^2 = \left(\frac{\partial x}{\partial \omega}\right)^2 \sigma_\omega^2 \\
\sigma_x^2 = \frac{1}{4} \omega^{-3} \sigma_\omega^2
\]
5. Possible explanations for the higher HER rate on G/Pt(111) than Pt(111)

5.1. Electronic effects
One possible explanation for the increase in HER currents on G/Pt(111) electrodes is electronic effects. For instance, a weaker $\text{H}^+$ adsorption is predicted to decrease barriers for HER. In addition, it is also possible that various impurities and functional groups at graphene defects conjugate and change the electronic properties of graphene or Pt(111).

5.2. Structural effects
Structural effects is another possible explanation for the increased HER currents. Physical confinement can lead to van der Waals stabilization, resulting in different orientations and geometries that may lead to different catalytic rates. We also cannot rule out the possibility of the graphene domain boundaries acting as a molecular one-way valve, allowing H$_2$ bubbles to transport out of the graphene-Pt(111) interstitial space.

5.3. Electrolyte effects
We have shown that strongly adsorbing anions can reduce the rate of H$_{\text{UPD}}$ even if there is no clear anion adsorption feature. This suggests that anions can block the access of protons to the defects. We have not studied their effect on HER rate in detail but we expect that they may have a similar effect.

5.4. Mass-transport effects
It is also possible that graphene with a high level of defects suppresses H$_2$ bubble formation, leading to higher HER rates G/Pt(111) electrodes.

5.5. Impurity effects
Impurities in our electrolyte from the H$_2$SO$_4$ stock solution or counter electrode may adsorb and coordinate to graphene, increasing the number of sites that are able to catalyze HER.

5.6. Free energy of $\text{H}^+$ adsorption on Pt(111) with and without graphene and its possible influence
Li et al. demonstrated using a series of DFT computations that the presence of graphene overlayers on a number of substrates (including Pt(111)) and adsorbates (including $\text{H}^+$) weakens the free energy of adsorption. Greeley et al. used DFT screening and demonstrated that
computed Gibbs free energy of absorption of H for a number of metal surfaces result in a volcano-type plot with closest to the top when compared to experimental HER current\textsuperscript{46-49}. Combining the predicted shift in H binding energy on Pt(111) from Li et al.\textsuperscript{34} with the volcano-type plot in Greeley et al.\textsuperscript{46} and our experimentally measured currents (Pt(111) red hollow circle and G/Pt(111) blue hollow circle in Figure S23) suggests that the increase in measured currents observed between Pt(111) and G/Pt(111) can potentially be explained by graphene overlayers weakening the H Gibbs free energy of absorption. It should be noted that even though this explanation could explain the increase in HER currents after addition of graphene overlayers on Pt(111), it does not rule out the possibility of other explanations listed in the previous section.

\textbf{Figure S23:} Presence of a graphene overlayer weakens H$^+$-Pt free energy of adsorption (Li et al.\textsuperscript{50}), shifting it closer to the optimum value of 0 eV. Free energy of H$^+$ adsorption were computed at 1/4 to 1/3 ML coverage\textsuperscript{46,50}. Our experimentally measured currents on Pt(111) (red hollow circle) and G/Pt(111) (blue hollow circle) suggests that the increase in measured currents observed between Pt(111) and G/Pt(111) can potentially be explained by a weakening of the H-Pt free energy of adsorption.
6. Imaging Results

6.1. SEM protocols and imaging locations on disks

To avoid bias in acquisition and analysis, five random pairs of angles between 0 and 360° and radii between 0 to 3.5 mm (for a 7 mm diameter disk) or between 0 and 5 mm (for a 10 mm diameter disk) with the constraint that no two points can be 0.5 mm from each other was generated.\(^{51,52}\)

6.2. Fraction of exposed monolayer do not significantly change after electrochemical pretreatment and after HER on G/Pt(111)

Post-processing SEM images with the colormap MATLAB function was used to quantify the effect of electrochemical pretreatments (cycle 250 times between 0.10 and 1.20 V\(_{\text{RHE}}\) at a rate of 500 V min\(^{-1}\) in 0.005 M H\(_2\)SO\(_4\)) and HER (exposure to overpotentials between 0.00 and -0.10 V\(_{\text{RHE}}\) in 0.005 to 0.5 M H\(_2\)SO\(_4\)) on graphene overlayers. SEM images taken at the five randomly generated points as described in the previous section at 1000x magnification were chosen due to a balance between resolution and area. Applying Equation S17 to the SEM images taken at random locations and plotting \(f_{\text{monolayer}}\) after before pretreatment, after pretreatment, and after HER (Figures S24 to S27) demonstrate that we do not observe changes in the fraction of exposed graphene monolayers on pretreated G/Pt(111) throughout HER.

\[
f_{\text{monolayer}} = \frac{\text{# white pixels}}{\text{total pixels}} \quad \text{(Equation S17)}
\]
**Figure S24:** SEM on G/Pt(111)#1 at 1000x magnification prior to electrochemical pretreatment or HER (left). MATLAB processed image (right) allows us to quantify the fraction of visible graphene monolayers in white.

**Figure S25:** SEM on G/Pt(111)#1 at 1000x magnification after electrochemical pretreatment and HER (left). MATLAB processed image (right) allows us to quantify the fraction of visible graphene monolayers in white.
Figure S26: Fraction of monolayer graphene on G/Pt(111)#1 on the as-synthesized electrode and after both electrochemical pretreatment and HER on five randomly imaged points each. Error bars are 2 times the standard deviation (~95% confidence).

Figure S27: Fraction of monolayer graphene on G/Pt(111)#2 on the as-synthesized electrode, after only electrochemical pretreatment and no HER, and after both electrochemical pretreatment and HER on five randomly imaged points each. Error bars are 2 times the standard deviation (~95% confidence).
6.3. Large defects suddenly appear after 10 hours after the anion adsorption coverage increases as indicated by CVs

Figure S28: SEM images of an electrode edge after 10 hours of HER on pretreated G/Pt(111) (left) and non-pretreated G/Pt(111) (right). It is possible that the dark splotch is a large crack that can allow the transport of $\text{SO}_4^{2-}$ and other anions into the space between graphene and Pt(111)
7. References


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(41) Bukowski, B. C.; Bates, J. S.; Gounder, R.; Greeley, J. Defect-Mediated Ordering of


