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# Hydrogen evolution intermediate in 2-dimensionally confined space between graphene and Au(111)

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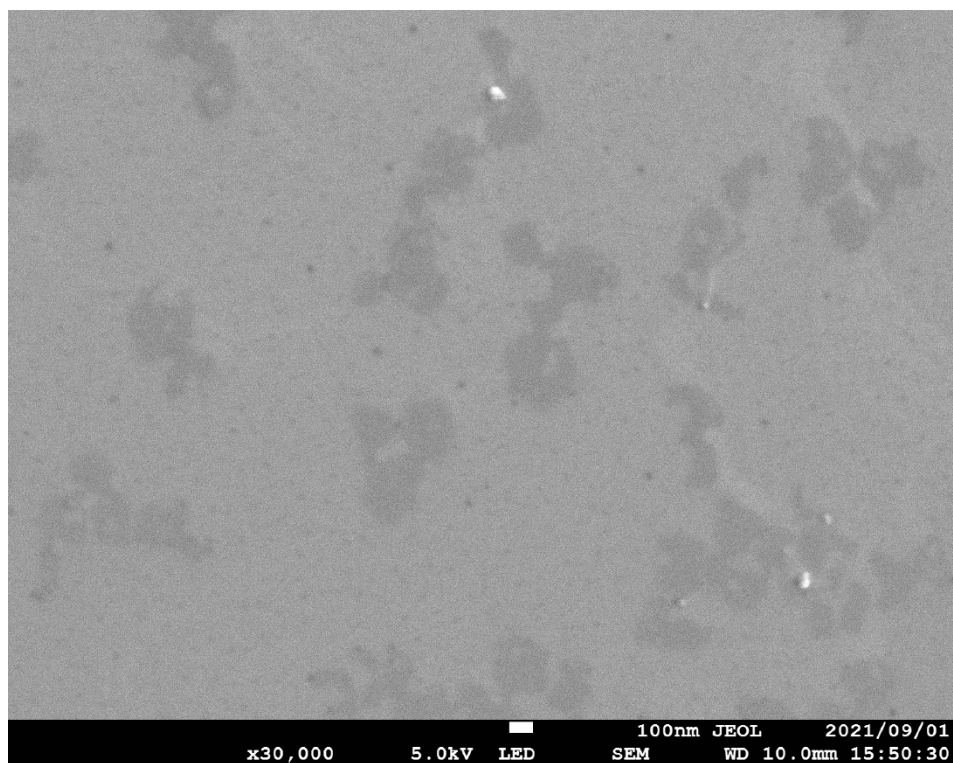


Figure S1. SEM image of Gr/Au(111)-0.5. The white rectangle at the bottom of the image is the scale bar for 100 nm.

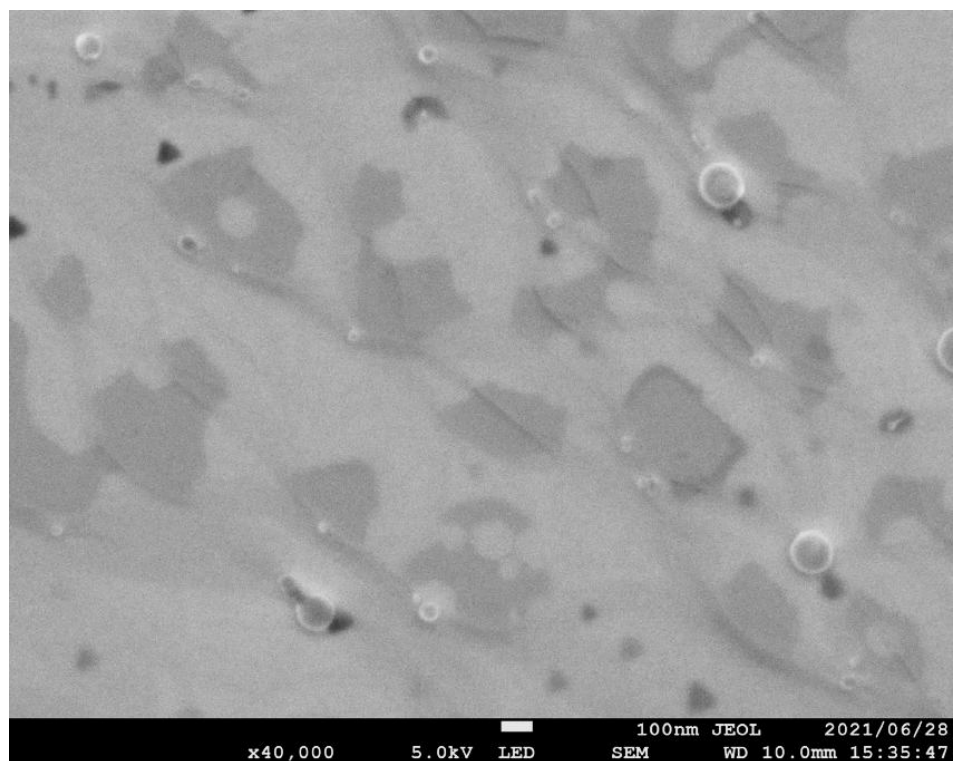


Figure S2. SEM image of Gr/Au(111)-2.

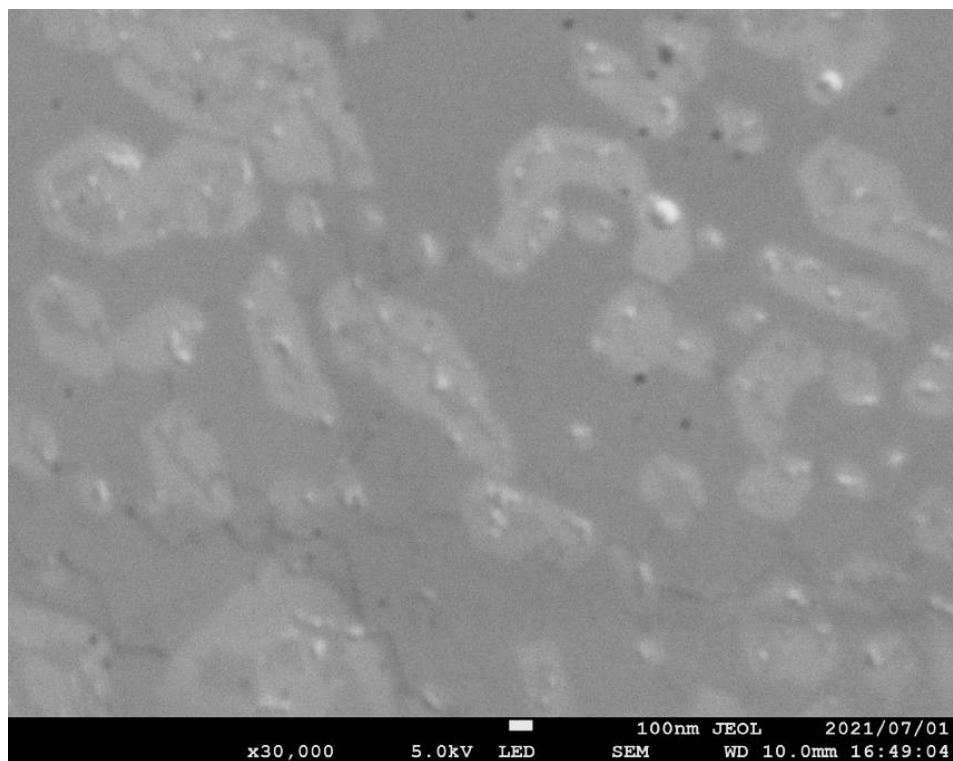


Figure S3. SEM image of Gr/Au(111)-4.

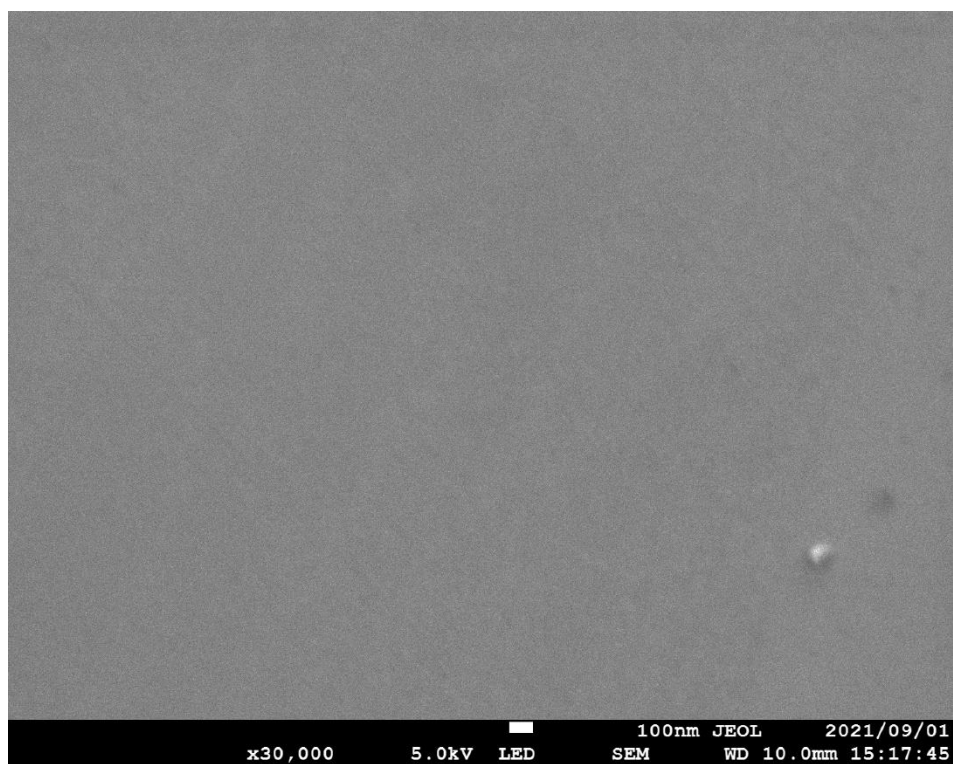


Figure S4. SEM image of Gr/Au(111)-8.

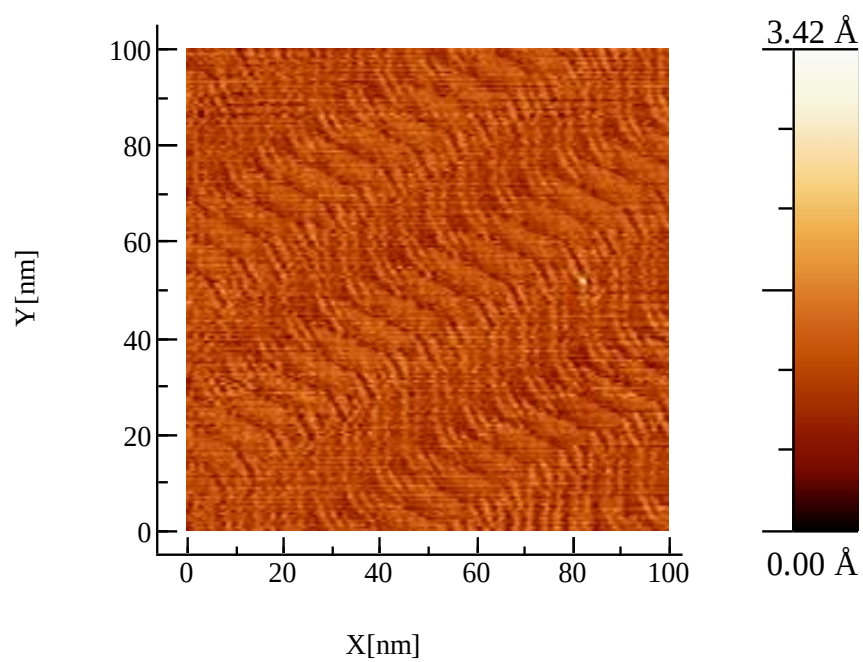


Figure S5. STM image of Gr/Au(111)-20.

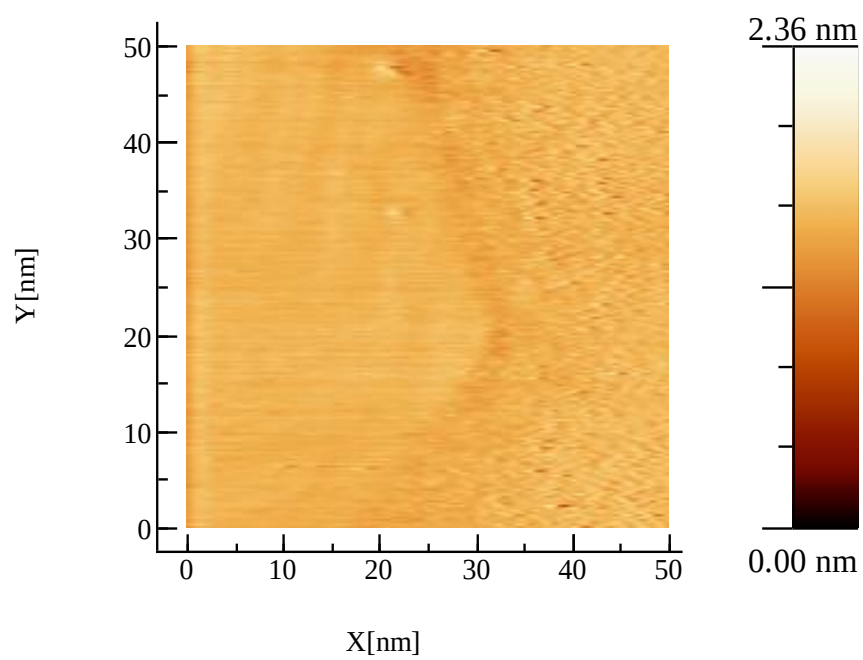


Figure S6. STM image of Gr/Au(111)-4 near the edge of graphene.

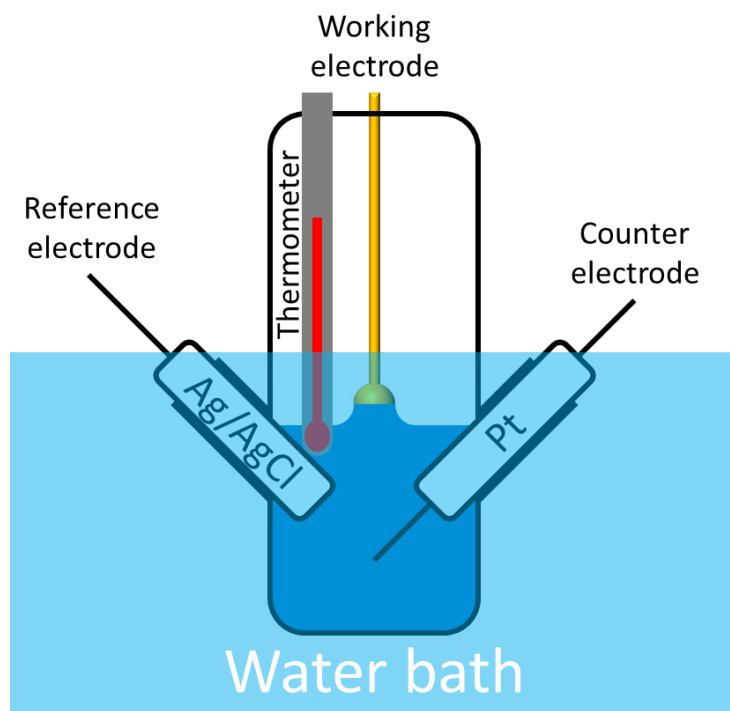


Figure S7. Cell for electrochemical measurements of Au(111) and Gr/Au(111).

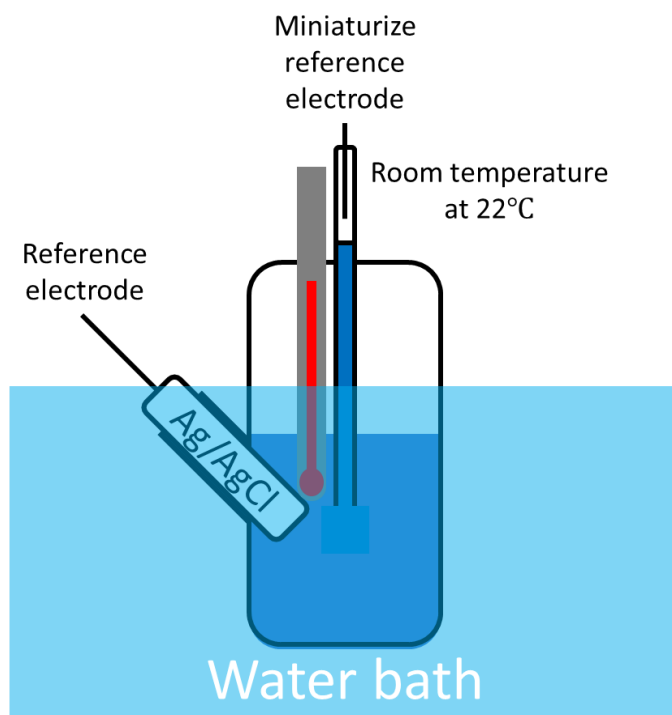


Figure S8. Cell for the calibration of reference electrode at varied temperatures.

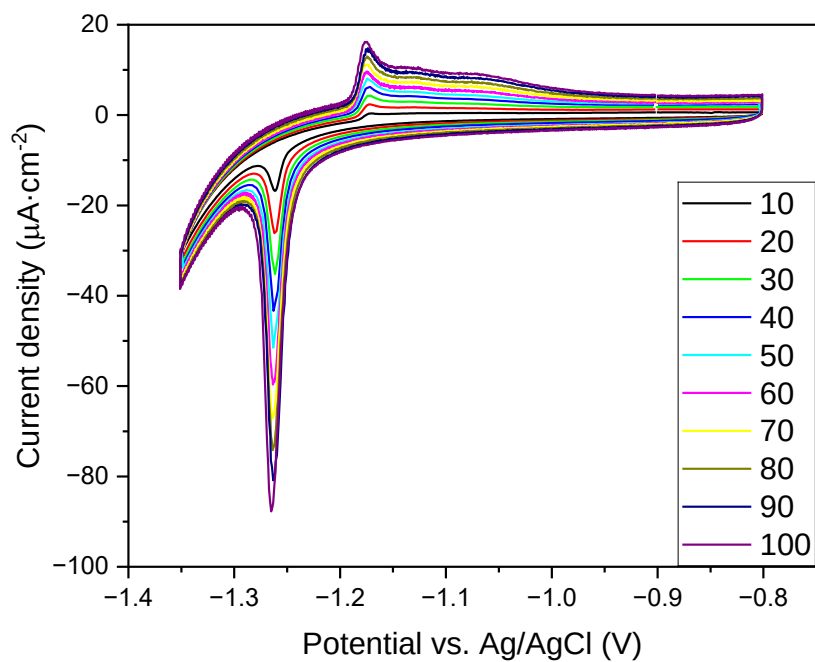


Figure S9. CV of Gr/Au(111)-20 in 0.1 M NaOH in H<sub>2</sub>O at various scan rates (mV·s<sup>-1</sup>).

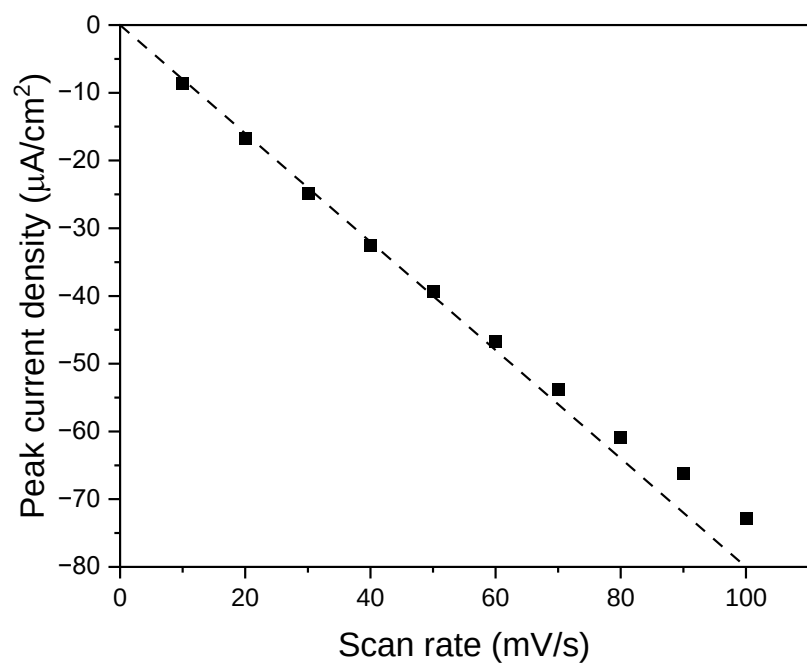


Figure S10. Cathodic peak current density of Gr/Au(111)-20 in 0.1 M NaOH in H<sub>2</sub>O vs scan rates.

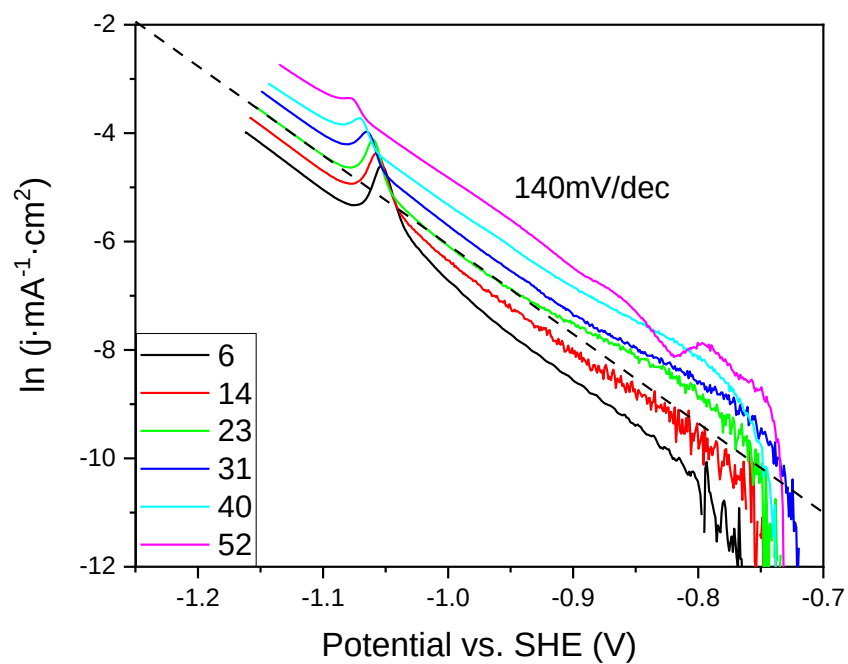


Figure S11. Tafel plots of HER on Au(111) in 0.1 M NaOH in H<sub>2</sub>O.  $j$  is the current density. The numbers in the legend are temperature in Celsius.

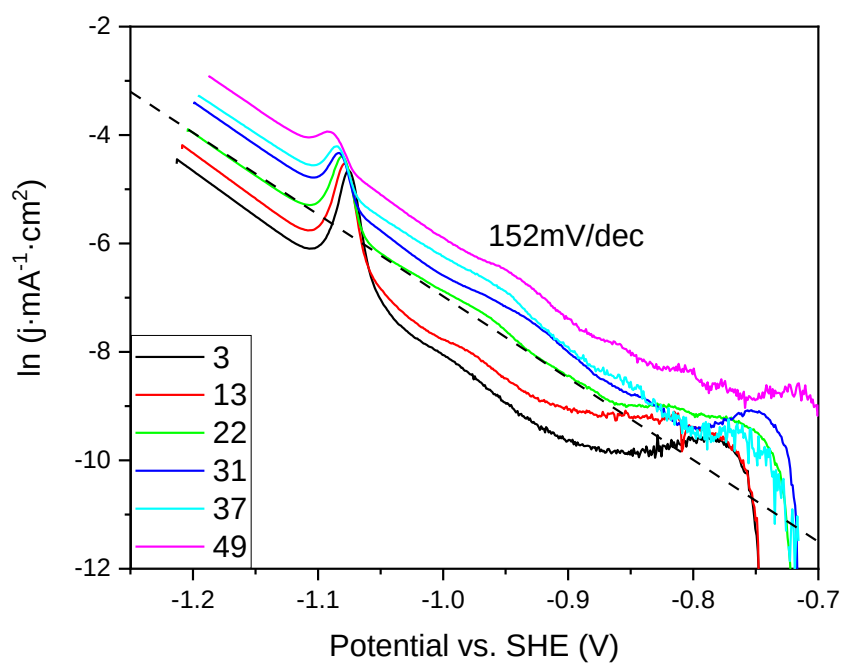


Figure S12. Tafel plots of HER on Gr/Au(111)-20 in 0.1M NaOH in H<sub>2</sub>O.

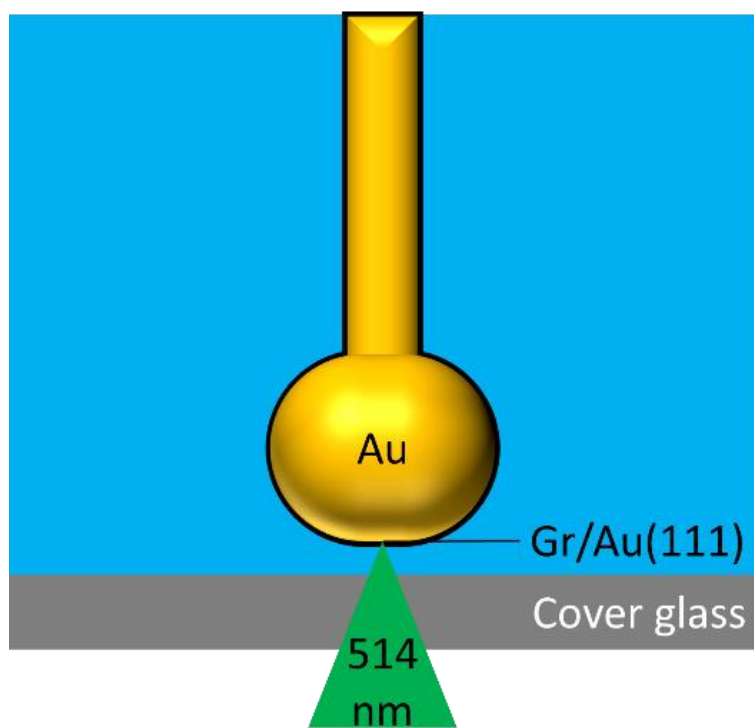


Figure S13. Setup for EC-Raman of Gr/Au(111).

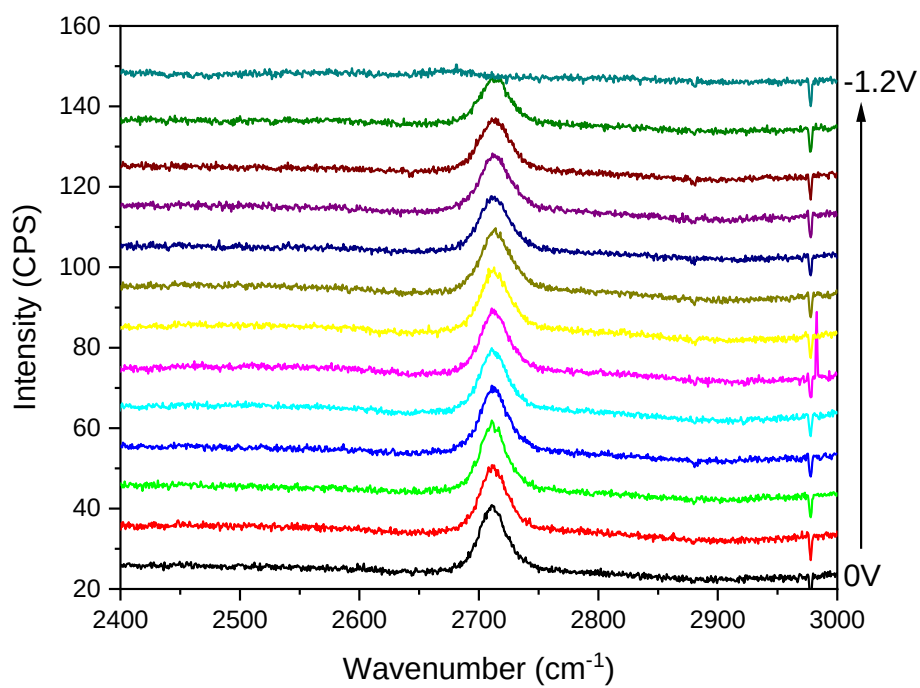
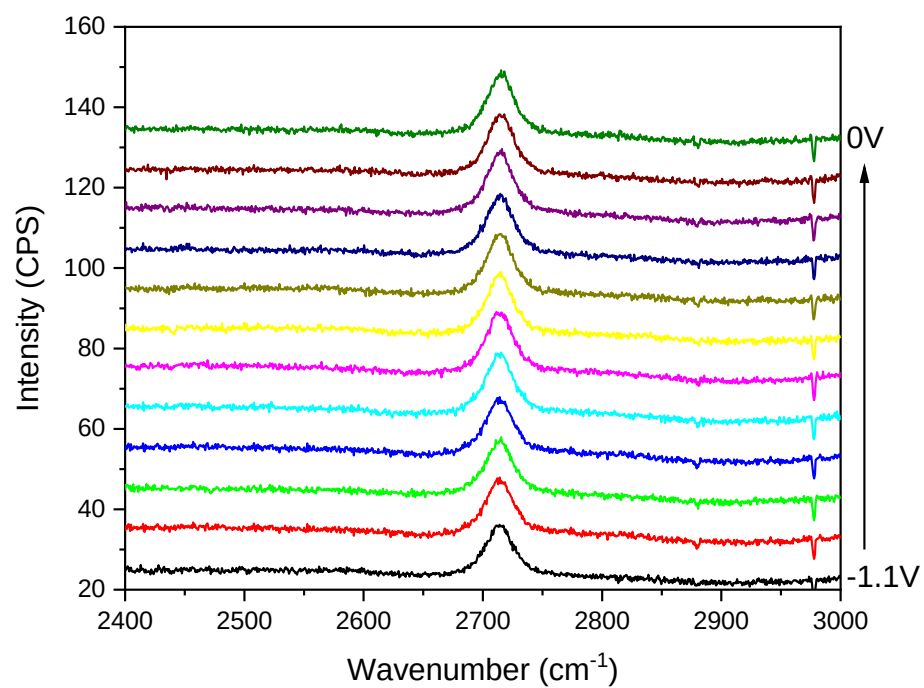


Figure S14. EC-Raman spectra of Gr/Au(111)-20 near 2700  $\text{cm}^{-1}$  in 0.1M NaOH in  $\text{H}_2\text{O}$ .

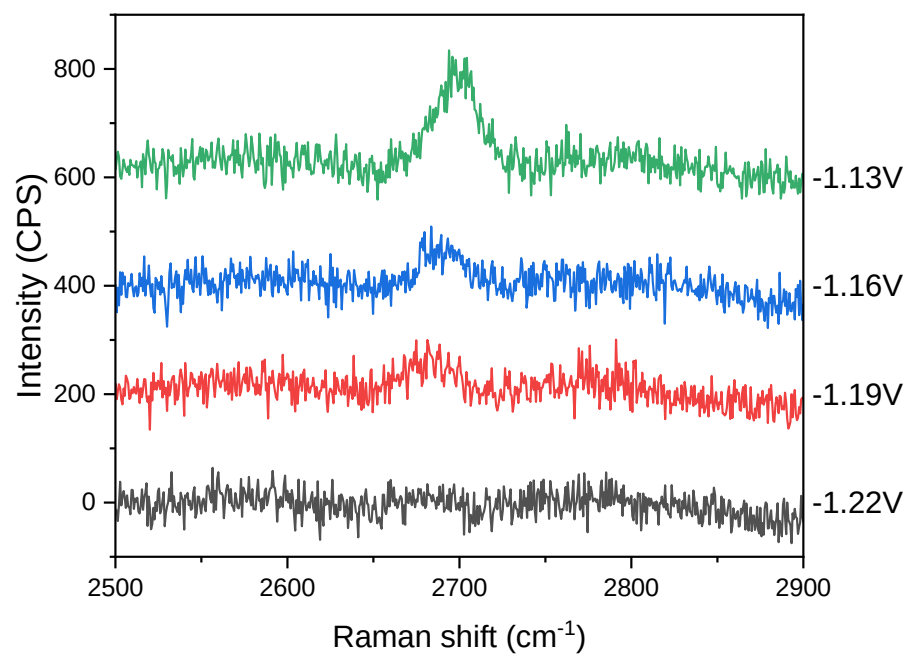


Figure S 15. EC-Raman spectra of Gr/Au(111)-20 near 2700 cm<sup>-1</sup> in 0.1M NaOH in H<sub>2</sub>O.

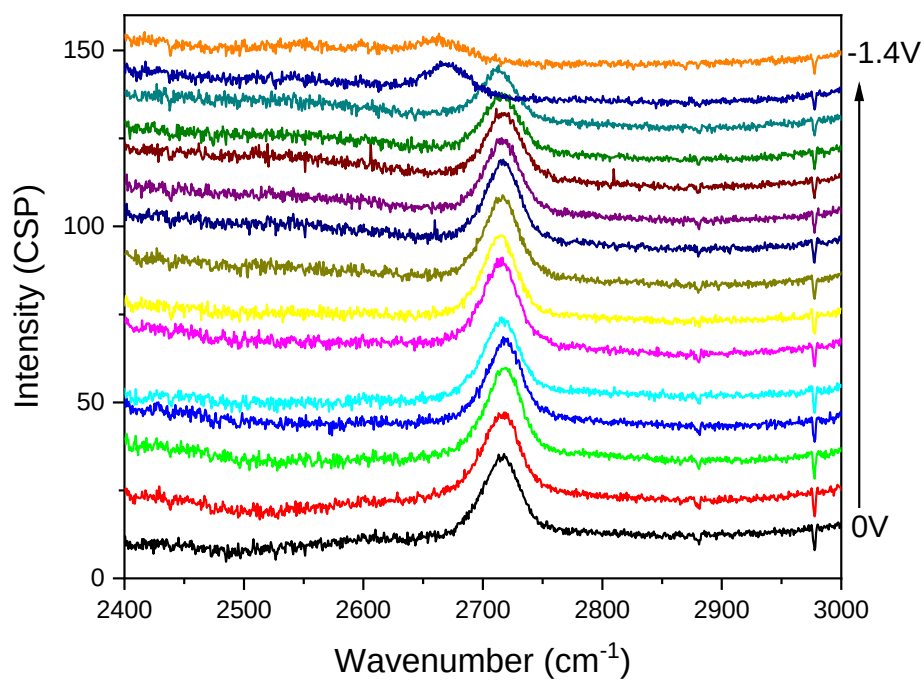
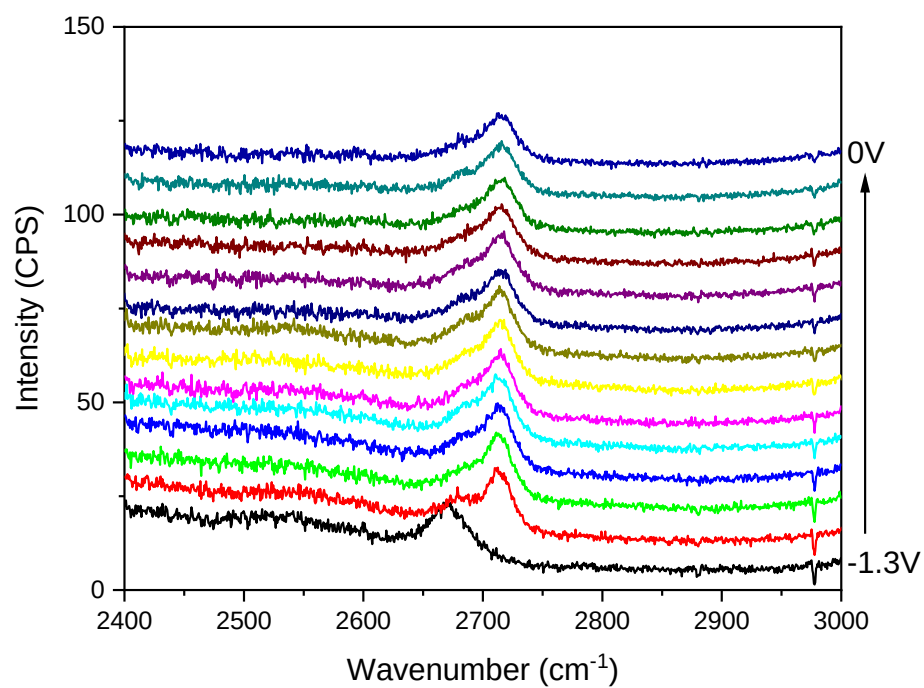


Figure S16 . EC-Raman spectra of Gr/Au(111)-20 near 2700 cm<sup>-1</sup> in 0.1M NaOD in D<sub>2</sub>O.

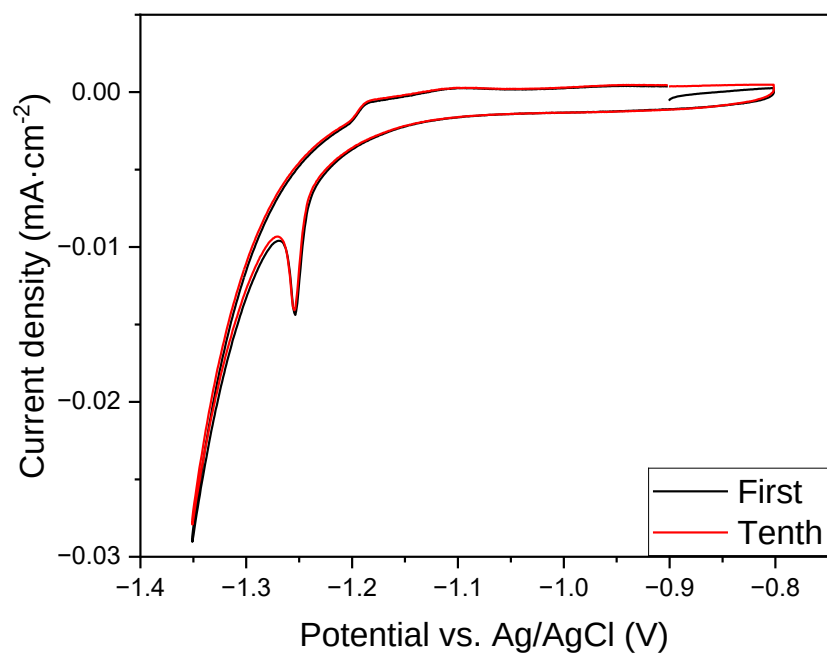


Figure S17. CV of Gr/Au(111)-20 of the first and tenth cycles.

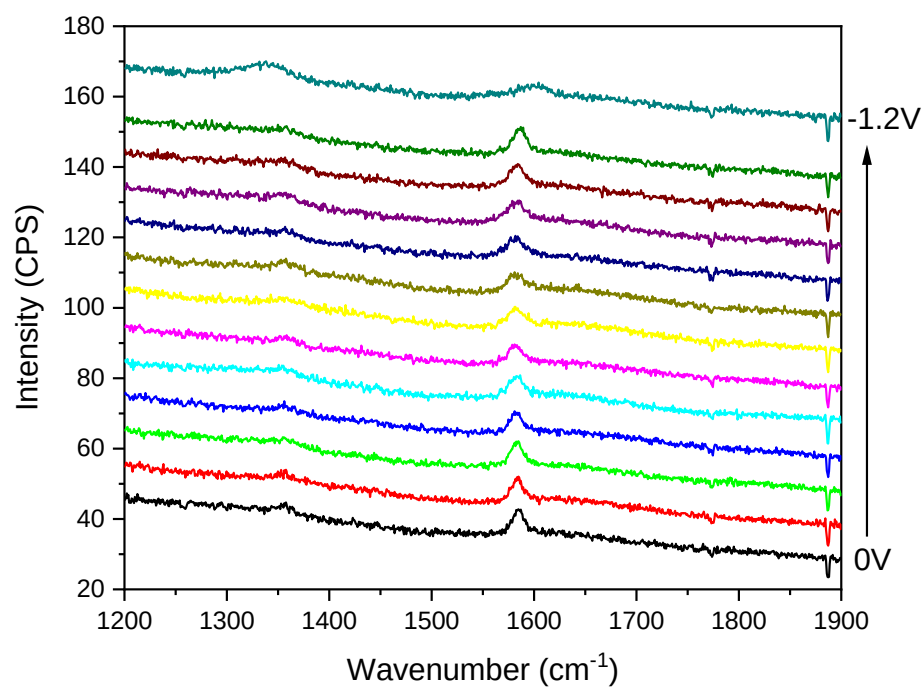
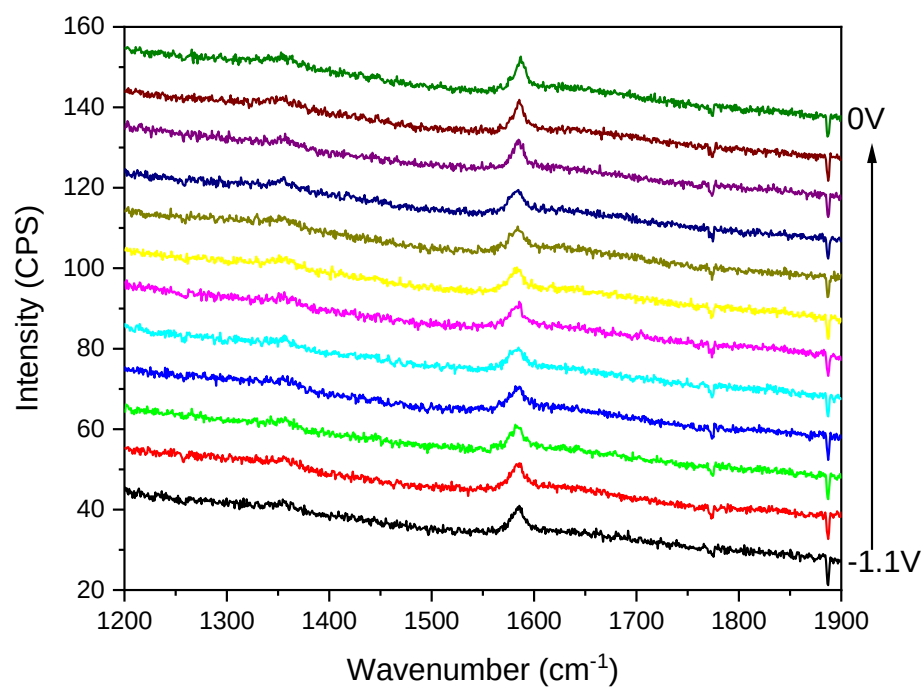


Figure S18. EC-Raman spectra of Gr/Au(111)-20 near 1600 cm<sup>-1</sup> in 0.1M NaOH in H<sub>2</sub>O from 0 V to -1.2 V potential vs Ag/AgCl.

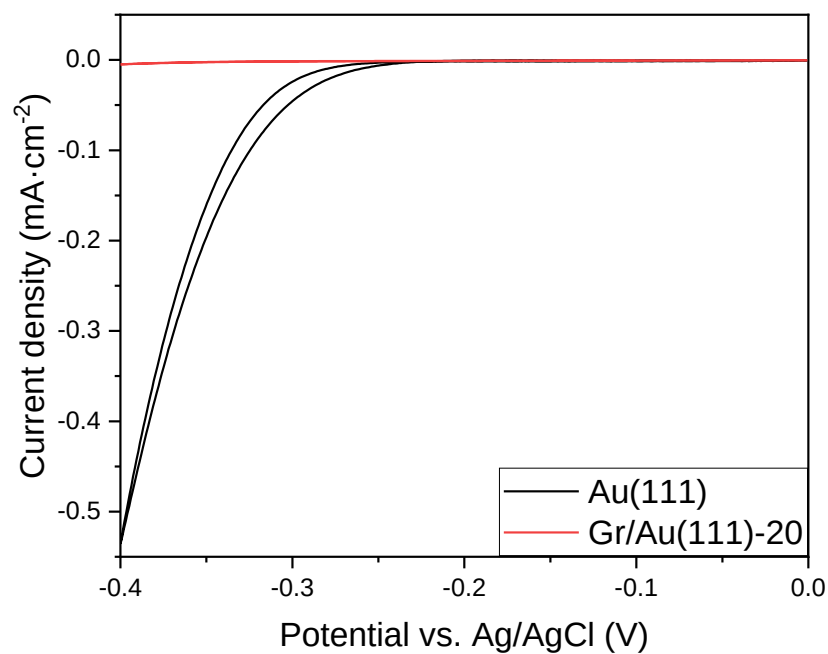


Figure S19. CV of Au(111) and Gr/Au(111) in 0.05 M H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O.

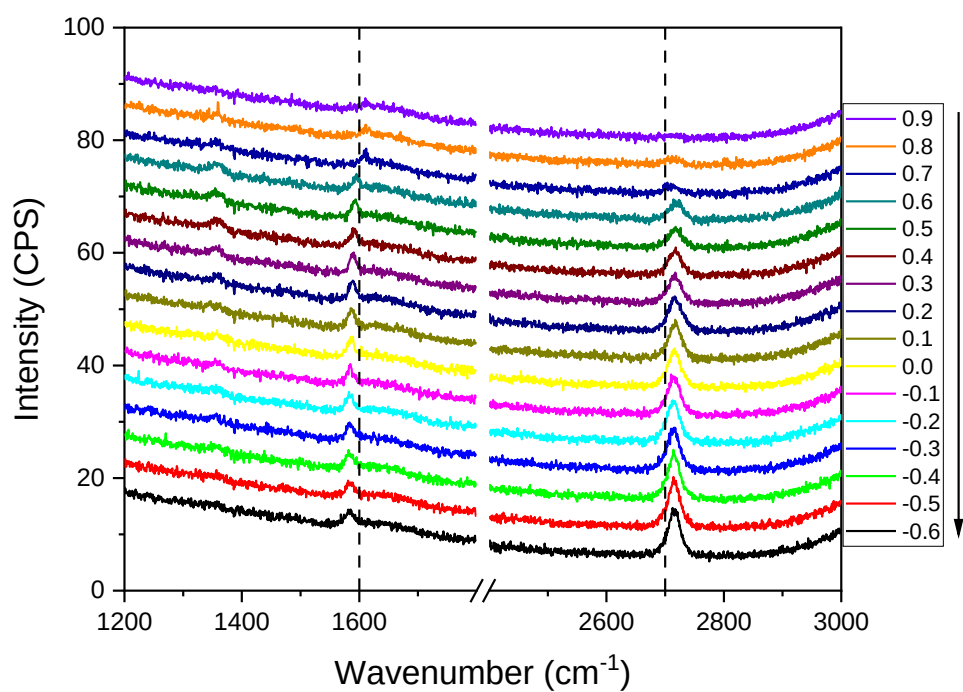


Figure S20. EC-Raman spectra of Gr/Au(111)-20 in 0.05 M H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O at various potentials vs Ag/AgCl (V).

### Calculation of activation energy

The calculation of activation energy is based on Arrhenius equation.

$$j_0 = ke^{-\frac{E_a}{RT}}$$

Here,  $j_0$  is the exchange current density. This equation can be rearranged to the following form.

$$\ln \frac{j_0}{j^\circ} = \ln \frac{k}{j^\circ} - \frac{E_a}{RT}$$

$j^\circ$  is selected to be  $1 \text{ mA} \cdot \text{cm}^{-2}$ . Then,  $E_a$  can be found by linear fitting  $\ln \frac{j_0}{j^\circ}$  vs  $\frac{1}{RT}$ .

To find  $j_0$ , Tafel equation is used.

$$\eta = -A \lg \frac{j}{j_0}$$

Here,  $\eta$  is overpotential, which is fixed to be -0.3 V vs. RHE.  $j$  is the current density at  $\eta$  from CV.  $A$  is the Tafel slope from figures S11 or S12.

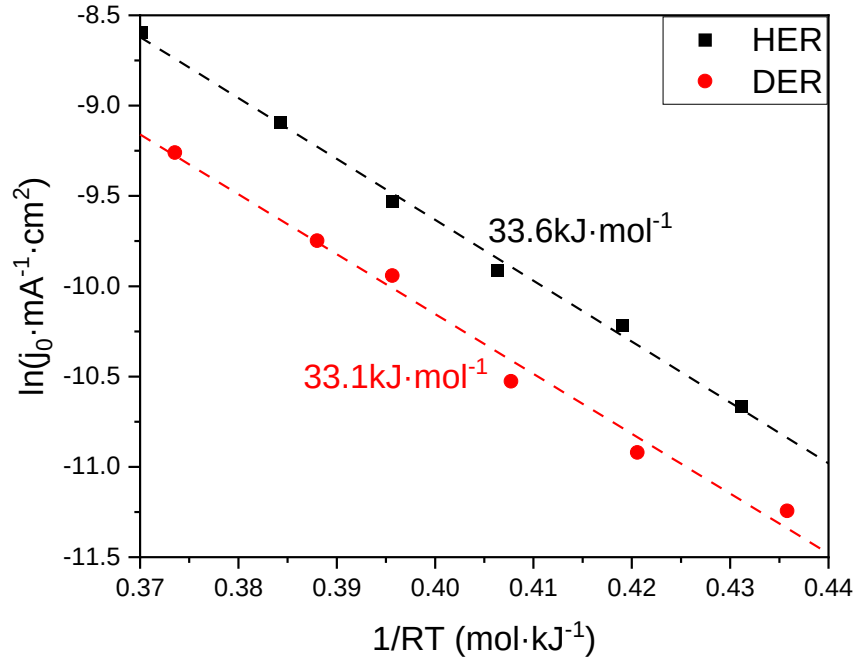


Figure S21. Arrhenius plots of HER and DER on Gr/Au(111)-20.

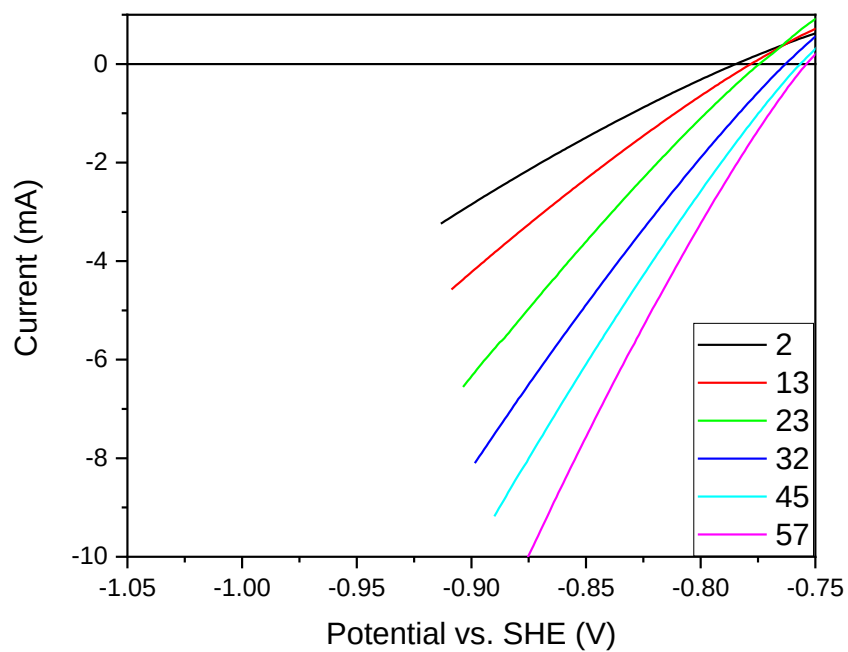


Figure S22. LSV of HER on Pt wire in 0.1 M NaOH in H<sub>2</sub>O.

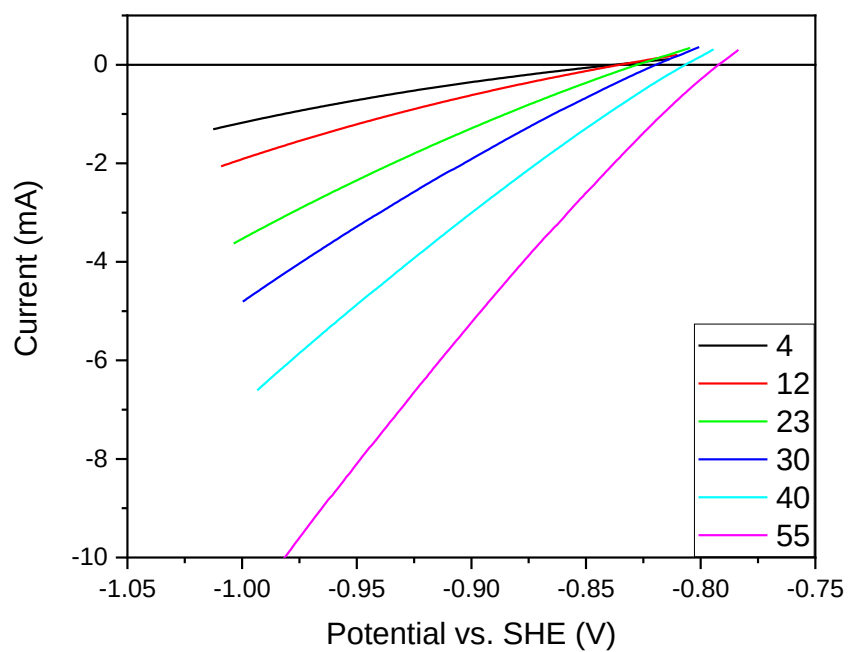


Figure S23. LSV of DER on Pt wire in 0.1 M NaOD in D<sub>2</sub>O.

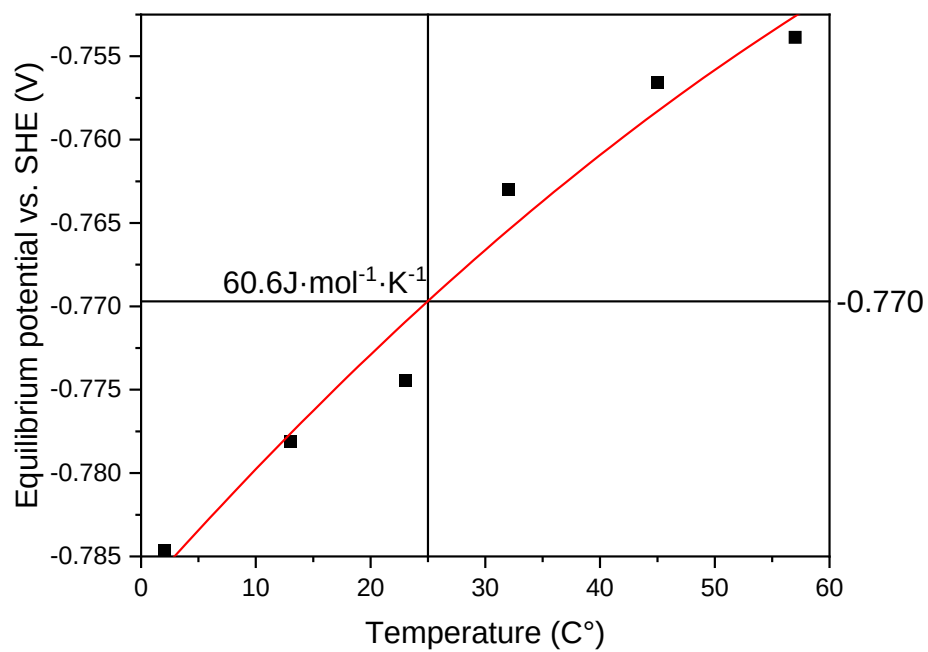


Figure S24.  $E(H_2O/H_2)$  vs. temperature in 0.1 M NaOH in  $H_2O$ .

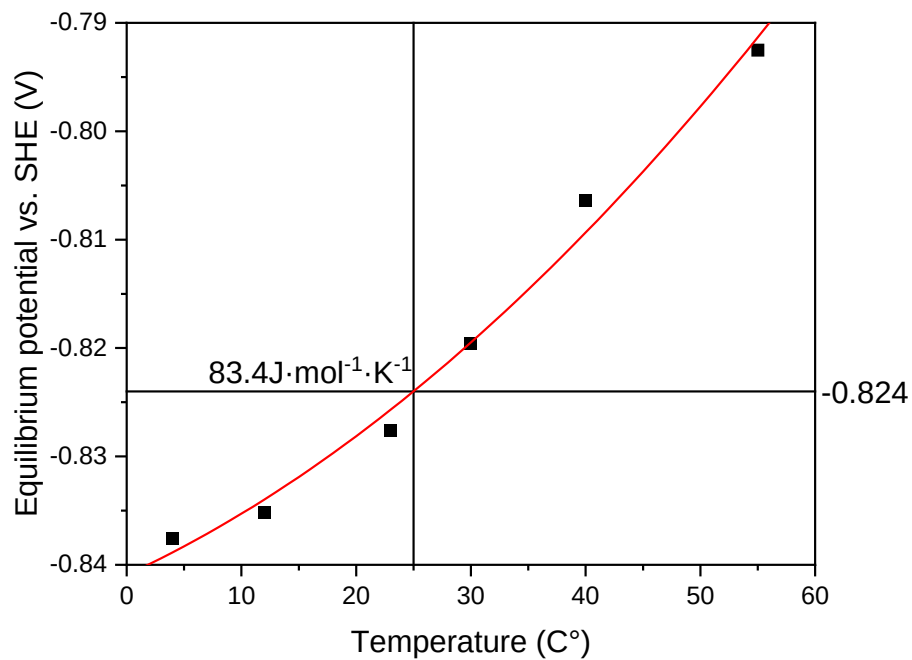


Figure S25.  $E(D_2O/D_2)$  vs. temperature in 0.1 M NaOD in  $D_2O$ .

### Calculation of the entropy of 2-dimensional atomic gas

In the calculation of entropy of 2-dimensional atomic gas, we used the 2-dimensional quantum box model, which successfully predicts the entropies of inert gases (Sackur-Tetrode equation).

In a 2-dimensional quantum box with length  $l$ , the Schrödinger equation of a particle is

$$-\frac{\hbar^2}{2m} \nabla^2 \left( \frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} \right) \psi = E\psi$$

The solution is

$$\psi = \frac{2}{l} \sin\left(\frac{n_x \pi}{l} x\right) \sin\left(\frac{n_y \pi}{l} y\right) \frac{2}{l} = \sin(k_x x) \sin(k_y y)$$

Where,

$$n_x, n_y \in \mathbb{Z}^+$$

$$k_x = \frac{n_x \pi}{l}, k_y = \frac{n_y \pi}{l}$$

The energies are

$$E = \frac{\pi^2 \hbar^2}{2ml^2} (n_x^2 + n_y^2) = \frac{\hbar^2}{2m} (k_x^2 + k_y^2) = \frac{k^2 \hbar^2}{2m}$$

Where,

$$k^2 = k_x^2 + k_y^2$$

The states are red dots in figure S. Each state occupies area  $\left(\frac{\pi}{l}\right)^2$  in the k-space.

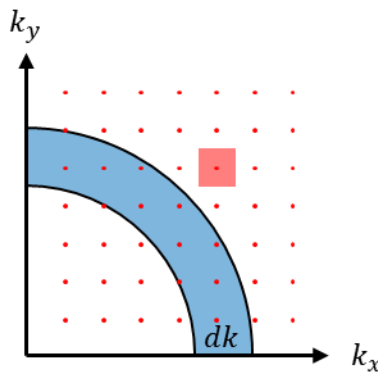


Figure S26. The states in k-space of 2-dimensional quantum box.

Suppose  $g$  is the energy degeneracy.  $gdE$  is the number of states in the 1/4 circular shell in the k space.

$$gdE = \frac{\frac{1}{2}\pi k dk}{\left(\frac{\pi}{l}\right)^2} = \frac{Ak dk}{2\pi}$$

$$g = \frac{Ak dk}{2\pi dE} = \frac{Am}{2\pi\hbar^2}$$

The partition function is

$$q = \int_0^\infty g e^{-\beta E} = \frac{Am}{2\pi\hbar^2} \int_0^\infty e^{-\frac{E}{k_B T}} dE = \frac{Amk_B T}{2\pi\hbar^2} = \frac{Am}{2\pi\hbar^2\beta}$$

The internal energy is

$$U = -N \frac{\partial \ln q}{\partial \beta} = Nk_B T$$

The entropy is

$$S = k_B \left(1 - \ln \frac{N}{q}\right) N + \frac{U}{T} = k_B \left(1 - \ln \frac{N}{\frac{Amk_B T}{2\pi\hbar^2}}\right) N + \frac{Nk_B T}{T} = 2Nk_B - Nk_B \ln \frac{2N\pi\hbar^2}{Amk_B T}$$

$$= 2nR + nR \ln \frac{mk_B T}{2\rho\pi\hbar^2}$$

$\rho$  is the number density of particles.  $\rho$  of H\* and D\* are calculated from the cathodic peak in the CV. They are  $7.2 \times 10^{17} \text{m}^{-2}$  and  $6.3 \times 10^{17} \text{m}^{-2}$ , respectively. Therefore, the calculated entropies of H\* and D\* 2-dimensional gases are  $58.4 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$  and  $65.3 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$ , respectively.