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

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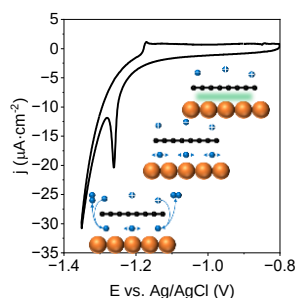
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ABSTRACT

Graphene-covered Au(111), Gr/Au(111), shows much better hydrogen evolution activity than bare Au(111) or graphene in alkaline electrolyte. It is due to a new state of hydrogen confined between graphene and Au(111). According to cyclic voltammetry, electrochemical Raman spectroscopy and scanning tunnelling microscopy measurement, when Gr/Au(111) is biased to a potential lower

than the $\text{H}_2\text{O}/\text{H}_2$ electrode potential, hydrogen deposits into the space between Au(111) and graphene. The Gibbs energy and entropy of hydrogen deposition are measured using the temperature-controlled cyclic voltammetry. Statistical mechanics calculation suggests that hydrogen forms 2-dimensional atoms gas in the 2-dimensional space between Au(111) and graphene which serves as a space-confined reactor, while the hydrogen atoms inside it serve as the reaction intermediate. The edge of graphene is the active site for hydrogen evolution because on partially covered Gr/Au(111) is significantly better than that on fully covered Gr/Au(111).

TOC Graphic



Hydrogen is regarded one of the most promising future energy carriers. The research on hydrogen production, storage and conversion has attracted intensive attention in the last couple of decades.^{1,2} The understanding of the states of hydrogen during the storage and conversion processes is at the vital position of the development of new mechanisms and materials.³ For instance, in electrochemical hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR), the intermediate hydrogen atoms form adsorbate on the active sites of the surface of the electrocatalysts. Therefore, the hydrogen binding energy (HBE) of the electrocatalyst is considered the most important property which determines its performance.⁴⁻⁷ A lot of efforts have been

devoted to the design and synthesis of electrocatalysts with optimized HBEs, such as MoS₂ and doped carbon.^{8,9} When the HBE is negative, *e.g.*, Pt group metals, it can be easily measured from the underpotential deposition (UPD) of hydrogen because the UPD current is not interfered by HER and can be observed in cyclic voltammetry (CV).¹⁰ However, for a material with positive HBE such as Au, the overpotential deposition (OPD) of hydrogen and HER occurs simultaneously. Therefore, the OPD current cannot be easily observed by CV.¹¹ On the other hand, HBE, by itself, is not enough to fully unveil the HER/HOR mechanism and performance.^{12,13} Other factors, such as the pH and cations of the electrolytes, as well as OH binding energy, also affect HER/HOR performance.^{14,15} Therefore, more thermodynamic and kinetic parameters, such as the entropy of the intermediate and the activation energy of the reaction, are not only scientifically important but also crucial for HER/HOR in varied conditions such as in cold or hot environment.

From the material point of view, graphene-covered metals have attracted some attention recently.^{16–18} The graphene cover has two effects. First, graphene is more stable than most non-noble metals in the potential range of HER. Thus, it serves as a protection layer to reduce their corrosion.¹⁹ On the other hand, though graphene is permeable to protons²⁰, graphene-covered metal shows inferior HER performance to the bare metal because of the additional hydrogen penetration barrier, if only the metal beneath it is HER active.²¹ However, it is widely reported that graphene and metal substrates have electronic interaction.^{22–25} The physical/chemical properties of graphene-covered metals are different from both graphene and metal. Therefore, the graphene-metal system could have unexpected interaction with hydrogen and extraordinary HER performance. Theoretical study has reported enhanced HER performance of graphene-covered metals.²⁶ Experimental results also showed that hydrogen chemisorption on graphene can be carried out under mild conditions via a Pt-electrocatalyzed spillover-surface diffusion

chemisorption mechanism.²⁷ Hydrogen confined between graphene and Pt(111) has special properties²⁸ and graphene-covered Pt(111) has better HER performance than bare Pt(111) due to optimized HBE.²⁹ The same effect can be expected on other metals, but there is no report on graphene-converted weakly HER-active metals.

In this paper, we report enhanced HER on graphene-covered Au(111), Gr/Au(111), in alkaline electrolyte. In-situ electrochemical Raman spectroscopy, temperature-controlled cyclic voltammetry and theoretical calculation suggest that hydrogen is deposited between graphene and Au(111) and forms 2-dimensional atomic gas. The HBE of Gr/Au(111) is significantly lower than that of Au(111) or graphene. Furthermore, the edge of graphene is the entrance/exit of hydrogen which serves as HER active site. Therefore, partially covered Gr/Au(111) shows significantly better HER performance than fully covered graphene/Au(111).

Graphene was grown on Au(111) by chemical vapor deposition.³⁰ The Au(111) surface was prepared by melting Au wire and mechanical polishing. Then, the Au bead with (111) surface was placed in a quartz tube (15 mm inner diameter) and heated to 1030 °C in 1000 sccm Ar (99.999%) flow. Graphene was grown at 1030 °C for 0.5 to 20 minutes by adding 0.36 sccm CH₄ (99.99%) flow to the tube. The sample is then cooled to room temperature in the tube with Ar flow. For convenience, the Gr/Au(111) samples are labeled based on their growth durations in minute. For instance, Gr/Au(111)-4 is Gr/Au(111) grown for 4 minutes.

A scanning electron microscopy (SEM) image of Gr/Au(111)-1 is shown in Figure 1a. The graphene covers about 15% of Au(111). The graphene flakes with some holes are about 300 nm in sized. There are also flakes smaller than 10 nm, but they do not contribute to the coverage significantly. The scanning tunnelling microscopy (STM) image of the big flakes acquired in air

is shown in Figure 1b. It shows the graphene has small holes below 5 nm. The SEM images of Gr/Au(111)-0.5, Gr/Au(111)-2, Gr/Au(111)-4 and Gr/Au(111)-8 are shown in Figures S1 to S4. Obviously, the coverage of graphene on Au(111) depends on the duration of growth. The graphene coverage of Gr/Au(111)-2 is about 30%, and the flakes are bigger as well. The graphene coverage of Gr/Au(111)-4 further increases to about 60% and all the graphene flakes are connected. As for Gr/Au(111)-8 and Gr/Au(111)-20, the coverages from SEM images are about 100%. It suggests that the graphene growth is completed within 8 minutes. Only a single layer of graphene can be grown because the decomposition of CH₄ on graphene is self-limited. The STM image of Gr/Au(111)-20 shows the herring bone reconstruction of Au(111) (Figure S5), which indicates close contact between graphene and Au(111). The graphene edges (Figure S6) always have 120° angles with each other, suggesting armchair edge structure. The Raman spectrum of Gr/Au(111)-1 (Figure 1c) shows significant G and 2D bands of graphene, as well as strong baseline from Au due to electronic scattering. The 2D band is at around 2710 cm⁻¹, which is about 30 cm⁻¹ higher than that of graphene on dielectric substrates, indicating a strong electronic interaction between graphene and Au(111).²² Though graphene of Gr/Au(111)-1 has plenty of edges, the D band corresponding to the defects of graphene is unobservable. It suggests that the graphene has very low crystallographic defect density and the atoms on the edge contribute a small fraction (about 1 per 10⁶ atoms for a 100 nm flake) to the graphene.

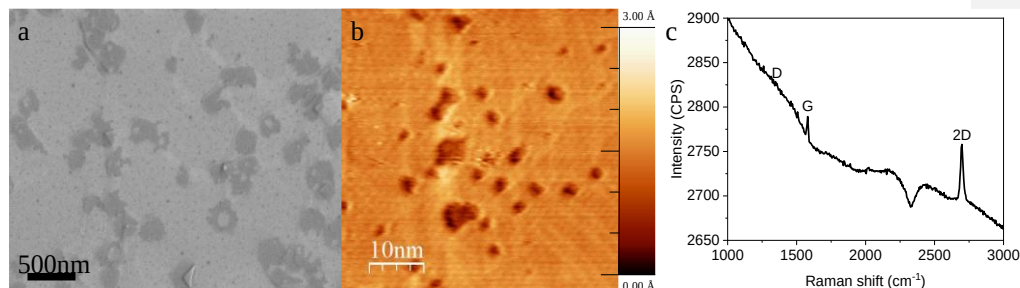


Figure 1. a) The SEM image of Gr/Au(111)-1. The darker part is graphene. b) The STM image of the graphene of Gr/Au(111)-1, showing the holes in graphene. c) The Raman spectrum of Gr/Au(111)-1 with 514 nm excitation laser.

The CV of Au(111) and Gr/Au(111) were conducted in 0.1 M NaOH (pH 13) or 0.05 M H₂SO₄ (pH 1) in H₂O and 0.1 M NaOD (pD 13) or 0.05 M D₂SO₄ in D₂O (pD 1) as electrolytes using an in-house built three-electrode cell (Figure S7). A Pt wire and a Ag/AgCl saturated KCl electrode were used as the counter and reference electrodes, respectively. The electrolyte was bubbled with Ar gas (99.999%) to deoxygenate for 20 min before experiment. The working electrode was suspended above the electrolyte level so that only Gr/Au(111) was measured. A thermometer was placed close to the working electrode and reference electrode to monitor their temperature. The measurements were conducted between 5 °C and 50 °C in a water bath. The reference electrode was then calibrated to standard hydrogen electrode (SHE) with another reference electrode at room temperature (22 °C) connected to the electrolyte with a thin channel (Figure S8).

The CVs of Au(111) and Gr/Au(111) in pH 13 electrolyte are shown in Figure 2a. The equilibrium potential of H₂O/H₂, $E(\text{H}_2\text{O}/\text{H}_2)$, is about -0.97 V vs. Ag/AgCl. It is obvious that HER on bare Au(111) is very slow. With graphene cover, HER performance improves significantly. The fully covered Gr/Au(111)-20 shows 4.4 times HER current density of Au(111) at -1.35 V. This result

is unexpected because graphene is a worse HER electrocatalyst than Au.¹ It suggests that the HER catalysis mechanism on Gr/Au(111) is different from either graphene or Au(111).

Moreover, the Gr/Au(111) of shorter growth times (*i.e.*, lower coverages) show even better HER performance. Figure 2b shows the HER current densities at -1.35 V Gr/Au(111) with different coverages. Gr/Au(111)-1 has the highest current density, which is 36 times of the bare Au(111) and 8 times of the fully covered Gr/Au(111)-20. Since Gr/Au(111)-1 has much more graphene edge, it is believed that HER is enhanced at the edge on graphene rather than on its basal plane.

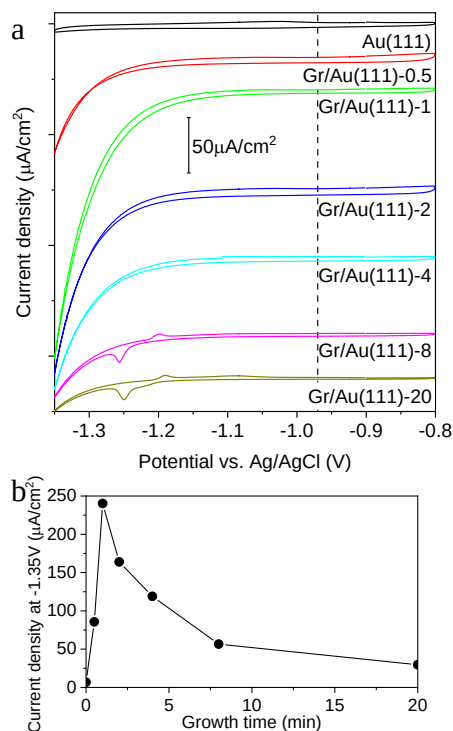


Figure 2. a) CVs of Au(111) and Gr/Au(111) in 0.1M NaOH aqueous solution (pH 13). The sweep rate is $5 \text{ mV}\cdot\text{s}^{-1}$. The dash line indicates the $\text{H}_2/\text{H}_2\text{O}$ equilibrium potential. b) HER current densities of different Gr/Au(111) at -1.35 V.

Another phenomenon worth taking note of is that, in the CV of Gr/Au(111)-8 and Gr/Au(111)-20, which have almost 100% graphene coverage, there is a significant cathodic peak, a lower anodic peak, and another even lower but much wide anodic peak. The CV of Gr/Au(111)-20 at varied scan rates were measured and shown in Figure S9. Neither the cathodic peak nor the anodic peaks shift with scan rate, suggesting fast electron transfer kinetics. Moreover, the cathodic peak current is almost proportional to the scan rate (Figure s10), suggesting simple deposition reaction without diffusion control. The total area of the anodic peaks is similar area to the cathodic peak. All these behaviors resemble the UPD of hydrogen on Pt-group metals. Therefore, the cathodic peak is attributed to the deposition of hydrogen. However, unlike on Pt-group metals, the deposition of hydrogen on Gr/Au(111) occurs at a more negative potential than H_2/H_2O electrode potential, so it is OPD rather than UPD. The half-cell reaction of UPD/OPD in alkaline electrolyte is the Volmer process denoted as reaction (a).



H^* is the hydrogen deposited on the electrode. The hydrogen is considered to be deposited between graphene and Au(111) and form 2-dimentional atomic gas, evidenced by in-situ Raman spectroscopy, STM images and entropy calculation discussed later.

The cathodic peak is at about $E_p = -1.26$ V (-0.29 V vs. reversible hydrogen electrode, RHE). The first anodic peak is at around -1.17 V. The second anodic peak extends from the first anodic peak to as high as -0.9 V. Therefore, the cathodic/andic peak separation is significantly higher than typical fast and reversible redox reaction (60 mV),³¹ suggesting that OPD hydrogen undergoes another transition to form some more stable states, such as chemically bonded hydrogen on graphene,²⁷ but it is not discussed in this paper because it is related to HOR rather than HER.

Figure 3a shows the CV of the Gr/Au(111)-20 in pD 13 electrolyte alongside with the CV in pH 13 electrolyte. The deuterium evolution reaction (DER) current is 40% of the HER at -1.35 V. Like in pH 13 electrolyte, there is a significant cathodic peak, a lower anodic peak and another very wide anodic peak. The potentials of the peaks are 0.016 V lower than those in pH 13 electrolyte.

It is widely accepted that the electrode potential of hydrogen deposition (E vs. RHE) is a descriptor for the HBE of the electrode. UPD of hydrogen corresponds to negative HBE (*e.g.*, Pt-group metals), while OPD of hydrogen corresponds to positive HBE (*e.g.*, Au, Ag, Cu and carbon). However, usually only UPD peaks are observable in CV because OPD hydrogen is unstable. At the potential where OPD takes place, deposited hydrogen quickly undergoes Tafel or Heyrovsky process to form H_2 . As a result, OPD current is overwhelmed by the HER current and can hardly be observed. Fortunately, OPD of Gr/Au(111)-20 and Gr/Au(111)-8 can be observed. A possible reason is that, though OPD hydrogen in Gr/Au(111) is thermodynamically unstable, its lifetime is relatively long. It must find a defect to escape because the hydrogen penetration barrier through the basal plane is too high (over 2.6 eV), while penetration through a defect is barrierless.³² So, the HER current on fully cover Gr/Au(111) is not very high and the OPD peaks are observable. On the other hand, on Gr/Au(111) with low coverage, the OPD current is low while the HER current is significantly higher. Hydrogen atoms are formed at the edge of graphene, and most of them directly combine to form hydrogen gas. Therefore, the OPD peaks are not observed.

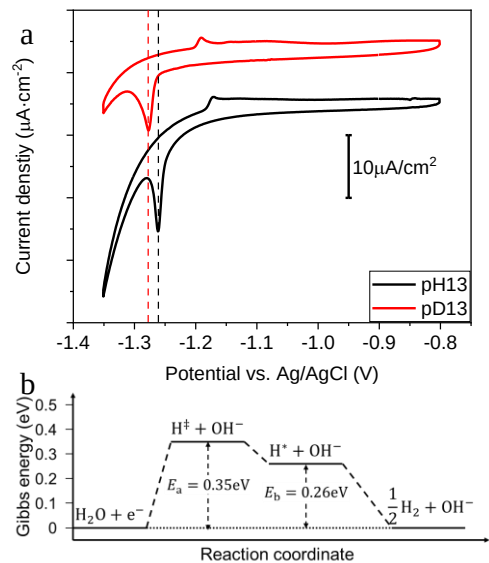


Figure 3. a) CVs of Gr/Au(111) in pH 13 and pD 13 electrolytes. The sweep rate is $5 \text{ mV} \cdot \text{s}^{-1}$. b) Gibbs energy diagram of HER on Au(111) and Gr/Au(111) at 0 V vs. RHE at room temperature. H^* is hydrogen deposited in Gr/Au(111). $\text{H}^\ddagger$ is the transition state between hydrogen in water and hydrogen in Gr/Au(111).

Since the kinetics of hydrogen OPD is fast, the cathodic peak potential is related to electrode potential (E) of reaction (a) by equation (1)³¹.

$$E = E_p + \frac{\ln(10)RT}{2F} \approx -0.26 \text{ V vs RHE} \quad (1)$$

Therefore, The HBE of Gr/Au(111)-20 is determined to be 0.26 eV. Though the hydrogen at the edge of graphene may not have the same energy as that under the graphene, they should be close. So, we take this value as the HBE of HER. For comparison, HBE of Au(111) is calculated to be $0.45 \sim 0.48 \text{ eV}$.⁴ HBE of graphene is even higher. A Gibbs energy diagram of HER on Au(111) and Gr/Au(111) is shown in Figure 3b. According to Sabatier principle, on catalysts with positive HBEs, lower HBE leads to better HER performance. Thus, better HER on Gr/Au(111) can be

attributed to its lower HBE. The Tafel slope (calculated based on Tafel plot of Figure S11) of HER on Gr/Au(111)-20 is 140 mV/dec. Such Tafel slope suggests that the catalysts have positive HBEs and the Volmer step is the rate determining step,³³ in accordance with our previous model. The Tafel slope of DER on Gr/Au(111)-20 (calculated based on Tafel plot of Figure S12) is 152 mV/dec, indicating a similar mechanism but slower kinetics.

The in-situ electrochemical Raman (EC-Raman) spectroscopy was measured with a homemade cell (Figure S13). The electrolytes and counter electrodes are the same. The working electrode was submerged in the solution with the Gr/Au(111) as close as possible to the glass window at the bottom of the cell. A reversed microscope Raman spectrometer was used to collect Raman spectra of the electrode surface. A 514 nm, 1.5 mW laser was used for 120 s for all measurements.

The EC-Raman spectra near 2700 cm^{-1} of Gr/Au(111)-20 in pH 13 electrolyte are shown in Figure S14 and S15. The 2D band wavenumber vs. potential plots are shown in Figure 4a. From 0 V to -1.1 V , the 2D band wavenumber does not change significantly. All of them have the same wavenumber as that measured in air (about 2710 cm^{-1}) due to Au-graphene electronic interaction. It shows that the graphene-Au(111) electronic interaction is preserved in this potential range. From -1.10 V to -1.20 V , there is a sharp drop of 2D band wavenumber to about 2680 cm^{-1} , as well as a significant intensity drop. For comparison, the 2D band wavenumber of graphene on ITO glass and dielectric substrates has a maximum at around 2685 cm^{-1} at -0.5 V and decreases gradually as potential further lowers.^{22,34} Therefore, the dramatic 2D band wavenumber drop should be attributed to the removal of graphene-Au(111) electronic interaction due to the increase of distance between them. When the potential rises back to above 1.1 V , the 2D band wavenumber rises back to about 2710 cm^{-1} . It suggests that the graphene-Au(111) electronic interaction is fully recovered because the distance between them is reduced to the original value. In pH 13 electrolyte, the 2D

band drops at about -1.3 V (Figure S16). In both pH 13 and pD 13 electrolytes, the potentials where 2D band wavenumber drop are the same as the potentials where OPD starts. Furthermore, the STM image of Gr/Au(111)-20 before electrochemical measurement (Figure 4b) shows significant moiré pattern due to the mismatch of graphene and Au(111) lattices.^{35,36} In contrast, Figure 4c shows the STM image of the same sample after electrochemical measurement, in which the moiré pattern is absent. The result shows that though the distance between graphene and Au(111) is recovered to the original value, the characteristic lattice mismatch due to CVD growth at high temperature is lost. Combining the EC-Raman and STM results, it is evident that the hydrogen is deposited between graphene and Au(111) during OPD. A schematic of hydrogen OPD on Gr/Au(111) is shown in Figure 4d. During OPD, the hydrogen atoms are deposited between the graphene and Au(111) through either the defect or the edge of graphene. The deposited atoms separate graphene and Au(111) and remove their electronic interaction. The CV of the first cycle is almost the same as the 10th cycle (Figure S17), suggesting that the OPD is reversible and causes no change to Gr/Au(111) except the lattice mismatch.

In addition to the separation of graphene and Au(111), the EC-Raman spectra of Gr/Au(111)-20 near 1600 cm^{-1} in pH 13 electrolyte (Figure S18) show an increase of D band intensity at -1.2 V. It suggests that some hydrogen atoms may form chemisorption on graphene after OPD, introducing defects to it. It is like the spillover of hydrogen from Pt to graphene.²⁷ It also explains the anodic peaks in CV.

The HER of Gr/Au(111) were also measured in acidic electrolyte ($0.05\text{ M H}_2\text{SO}_4$). In pH 1 electrolyte, the HER on Au(111) is over 100 times faster than that on Gr/Au(111)-20 (Figure S19). No redox peak was found in the CV of Gr/Au(111)-20. Meanwhile, even at potential as low as $-$

0.6 V (-0.31 V vs. RHE), where the HER is already very fast, no significant change in 2D band is observed (Figure S20). All these findings suggest that hydrogen OPD on Gr/Au(111) does not happen in acidic electrolyte. A possible reason for the difference between alkaline and acidic electrolytes is that in alkaline electrolyte, HER occurs at much lower absolute electrode potential (0.71 V lower in pH 13 electrolyte compared to pH 1 electrolyte). Thus, there is extra negative charge on Gr/Au(111) in alkaline electrolyte, which could lower the HBE of it. It could also give a hint to the long-lasting debate of the pH dependence of HBE and HER.^{5,12} At least for our Gr/Au(111), HBE is sensitive to pH and it has strong influence on HER performance.

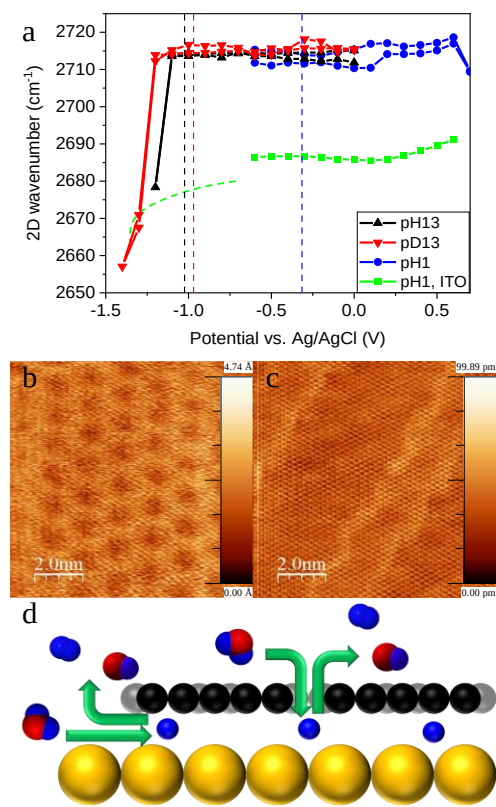


Figure 4. a) 2D band wavenumber vs. electrode potential in different electrolytes. Red, black, and blue dash lines: $E(H_2O/H_2)$ pH 13 electrolyte and $E(D_2O/D_2)$ in pD 13 electrolytes and $E(H_2O/H_2)$ in pH 1 electrolyte, respectively. Green dash line: projected 2D band wavenumber of graphene. b) and c) STM images of Gr/Au(111)-20 before and after electrochemical experiment. d) schematic drawing of hydrogen HER on Gr/Au(111). Golden, black, red, and blue spheres represent Au, C, O and H atoms, respectively.

To further understand the OPD and HER of Gr/Au(111), temperature-controlled CVs of Gr/Au(111)-20 were measured in pH 13 and pD 13 electrolytes. In this experiment, the reference electrode was kept at room temperature (22°C) and connected to the electrolyte via a thin tube. The exchange current densities at varied temperatures are calculated and Arrhenius equation is used to calculate activation energy (See details in SI and Figure S21). The activation energy of

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HER and DER on Gr/Au(111)-20 are both about $33\sim34\text{ kJ}\cdot\text{mol}^{-1}$, corresponding to a reaction barrier of $0.35\sim0.36\text{ eV}$. Such barriers are much lower than the proton penetration barrier through the basal plane of monolayer graphene obtained by calculation ($>1.2\text{ eV}$) or experiments ($\sim0.8\text{ eV}$)²⁰, which is not affected by Au^{20,37}. Hydrogen penetration has an even higher barrier.³² Thus, proton/hydrogen penetration is unlikely the rate determining step of HER. During HER, protons and hydrogen atoms should transfer through the defects and edge of graphene. This mechanism can explain higher HER activity of partially covered Gr/Au(111). The reaction barrier is most likely caused by the water dissociation in the Volmer step. A transition state hydrogen, $\text{H}^\ddagger$, with 0.35 eV Gibbs energy is shown in Figure 3b. Figure 5a shows the cathodic peak potential vs. temperature of Gr/Au(111)-20 in pH 13 and pD 13 electrolytes. Since the reference electrode was kept at a constant temperature, the temperature coefficients measured are “thermal”.³⁸ The potential of the peak is related to the isosteric Gibbs energy of OPD.

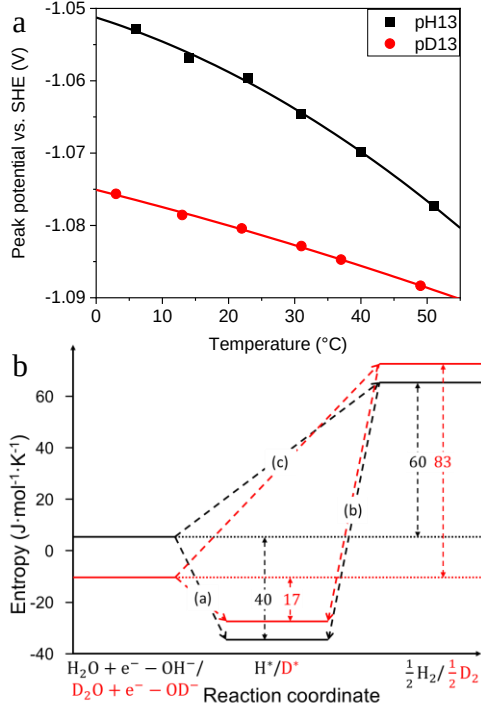


Figure 5. a) The cathodic peak potential vs. temperature of Gr/Au(111)-20 in pH 13 and pD 13 electrolytes. b) The entropy diagram of HER and DER, and OPD of H and D.

For one-electron reductive electrochemical reaction, $O + e^- \rightarrow R$, the Gibbs energy of half-reaction at constant pressure and electrode potential, E , is 0, as shown in equation (2).

$$\Delta_r G(E) = \Delta_r G(0V) + FE = \Delta_r H(0V) - T\Delta S + FE = 0 \quad (2)$$

Here, $\Delta_r G(0V)$ and $\Delta_r H(0V)$ are the isosteric Gibbs energy and isosteric enthalpy of half-reaction at 0 V. ΔS is the isosteric entropy of half-reaction, which is supposed to be potential independent. Then, ΔS can be calculated by combining equations (1) and (2).

$$\Delta S = F \left(\frac{\partial E}{\partial T} \right)_p = F \left(\frac{\partial E_p}{\partial T} \right)_p + 1.15R \quad (3)$$

ΔS calculated from the temperature coefficients of E_p in Figure 5a are $-40 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for hydrogen OPD and $-17 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for deuterium OPD at 25°C , respectively. However, these values are difficult to discuss because the absolute entropies of proton and deuterium in solutions are difficult to define. In comparison, the isosteric deposition entropies from the gas phases (H_2 and D_2), reaction (b), have very clear physical meaning because the absolute entropies of gases are well defined.



To find the entropy of reaction (b), the entropy of HER, reaction (c), is needed.



Obviously, reaction (a) is the sum of reactions (b) and (c). Therefore, the difference between the entropies of reactions (a) and (c) is the entropy of reaction (b). The entropy of HER is calculated using equation (3), with $E(\text{H}_2\text{O}/\text{H}_2)$ measured at various temperatures using linear scan voltammetry (LSV) of Pt wire in H_2 saturated pH 13 electrolyte (Figure S22). The same was done in D_2 saturated pD 13 electrolyte (Figure S23) to find the entropy of DER. The potentials of zero current in LSV are used as $E(\text{H}_2\text{O}/\text{H}_2)$ and $E(\text{D}_2\text{O}/\text{D}_2)$. The $E(\text{H}_2\text{O}/\text{H}_2)$ and $E(\text{D}_2\text{O}/\text{D}_2)$ vs. temperatures plots are shown in Figure S24 and S25. The calculated HER and DER entropies are $60 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $83 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. Therefore, the isosteric entropies of H_2 and D_2 deposition on Gr/Au(111)-20 are both $-100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The entropy diagram of HER and DER on Gr/Au(111) is shown in Figure 5b.

There are 2 significances of these entropies. First, the absolute entropies of $\frac{1}{2}\text{H}_2$ and $\frac{1}{2}\text{D}_2$ are $65.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $72.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. Thus, the “absolute entropies” of H^* and D^* are $-34.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $-27.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. The negative absolute entropies of H^* and D^* are because they are not pure substances. They only exist between graphene and Au(111). So, the entropies of H_2 and D_2 deposition are not only the result of the change of the states of H and D atoms but the change of whole system, including graphene and Au. According to theoretical calculation, the entropy of graphene increases when a gold atom is adsorbed on it.³⁹ Therefore, when H^* separates graphene and Au(111), the entropy of the Gr/Au(111) should decrease.

The second significance is that the entropy of H_2 deposition is identical to D_2 deposition. According to the principles in statistical mechanics, a heavier isotope has higher entropy than a lighter isotope in any form of motion. As the degrees of freedom of motion increase (*e.g.*, from adsorbate to gas), the difference in their entropies increases. So, identical entropy changes during H_2 and D_2 deposition suggests that H^* and D^* have the same degree of freedom as H_2 and D_2 . Therefore, H^* and D^* are not conventional adsorbates which attach to and vibrate at certain sites on the adsorbent. In contrast, H^* and D^* should move freely in the space between graphene and Au(111) like in gas phase. We suggest that they form 2-dimensional atomic gases. The entropy 2-dimensional atomic gas is calculated using statistical mechanics. The process is shown in SI. The result shows that 2-dimensional hydrogen and deuterium atomic gases of the areal concentrations in our experiment have entropies of $58.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $65.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. The entropy difference between H^* and D^* is $6.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which is close to the difference between $\frac{1}{2}\text{H}_2$ and $\frac{1}{2}\text{D}_2$ ($7.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). It explains why H_2 and D_2 depositions have almost identical entropy change.

The calculation of entropy by this method can suffer from some uncertainty. For example, though the thermometer, working electrode and reference electrode are kept in water bath, there is still a possibility of nonuniform temperature distribution. The working electrode on the top is surrounded by the atmosphere, which could be a little closer to the room temperature. So, the temperature range of the working electrode may be smaller than the measured range. This will cause the actual entropy to be higher than calculated. However, since all the experiments are carried out with the same setup, if all the entropies are slightly underestimated by the same margin, the qualitative conclusion should be the same.

There are very few studies on the H_2 deposition entropy on other metals. In theoretical calculation, it is usually considered to be only the loss of $\frac{1}{2}H_2$ entropy, *i.e.*, $-65.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ on all substrates.⁴ However, experimental studies show that hydrogen UPD entropy on Pt(111) in acidic electrolyte is about $-26 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.⁴⁰ Combining the fact that the HER entropy in acidic electrolyte is $81 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (from the fact that the HER temperature coefficient is $0.84 \text{ mV}\cdot\text{K}^{-1}$),⁴¹ it can be found that the entropy of $\frac{1}{2}H_2$ deposition on Pt(111) is $-107 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This entropy decrease is significantly greater than the $\frac{1}{2}H_2$ entropy because of the hardening of Pt crystal. DFT calculation also suggests that the deposited hydrogens on Pt move like 2-dimensional atomic gas and have the entropy of 2-dimensional atomic gas.⁴² These phenomena and theory are similar to our system suggesting that the formation of 2-dimensional atomic gas on Gr/Au(111) is possible.

The reason for the formation of 2-dimensional hydrogen atomic gas is still not fully understood. One possibility is the coupling between the graphene plasmon resonance and hydrogen at the interface. For example, it is recently reported that the confined hydrogen between silicon carbide and graphene shows the polaritonic interaction between plasmon and phonon mode.⁴³ Similar

system have been demonstrated with graphene and water, where the electronic temperature was cooled down with the interaction with water vibration modes, leading to the modification of the electronic structure of graphene and physicochemical properties of water.⁴⁴ The formation of 2-dimensional atomic gas between graphene and Au(111) can be explained with the polaritonic interaction. In fact, recently, it has been highlighted that the modification of the polaritonic interaction can lead to the modification of the properties of water.^{45–47} Graphene serves as nanospace for the condensation of hydrogen and polaritonic interaction through the graphene and Au(111) plasmon. This observed principle can be used for the HER acceleration by using graphene-covered metal systems.

In summary, Gr/Au(111) shows much better HER performance than graphene and Au(111) in alkaline electrolyte. It is attributed to its lower HBE than graphene and Au(111). When biased to low potentials, hydrogen atoms are deposited between graphene and Au(111) and form 2-dimensional atomic gas. The 2-dimensional hydrogen atomic gas serves as the active intermediate of HER. The edges of graphene on Gr/Au(111) are the entrance and exit for the hydrogen atoms as the HER active site. The reason for this deposition may be the coupling between graphene plasmon, gold plasmon and hydrogen. Our study also improves the understanding of the state of hydrogen confined in layered materials, which further promote the development of new HER and hydrogen storage materials.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

The calculation of activation energy and the entropy of 2-dimensional atomic gas.

Figure S1-S25: additional Figures as mentioned in the text. (PDF)

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Notes

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