

TUNING THE HYDROGEN EVOLUTION REACTION AT THE Pt(111) SURFACE WITH GRAPHENE AND NON-PRECIOUS METAL

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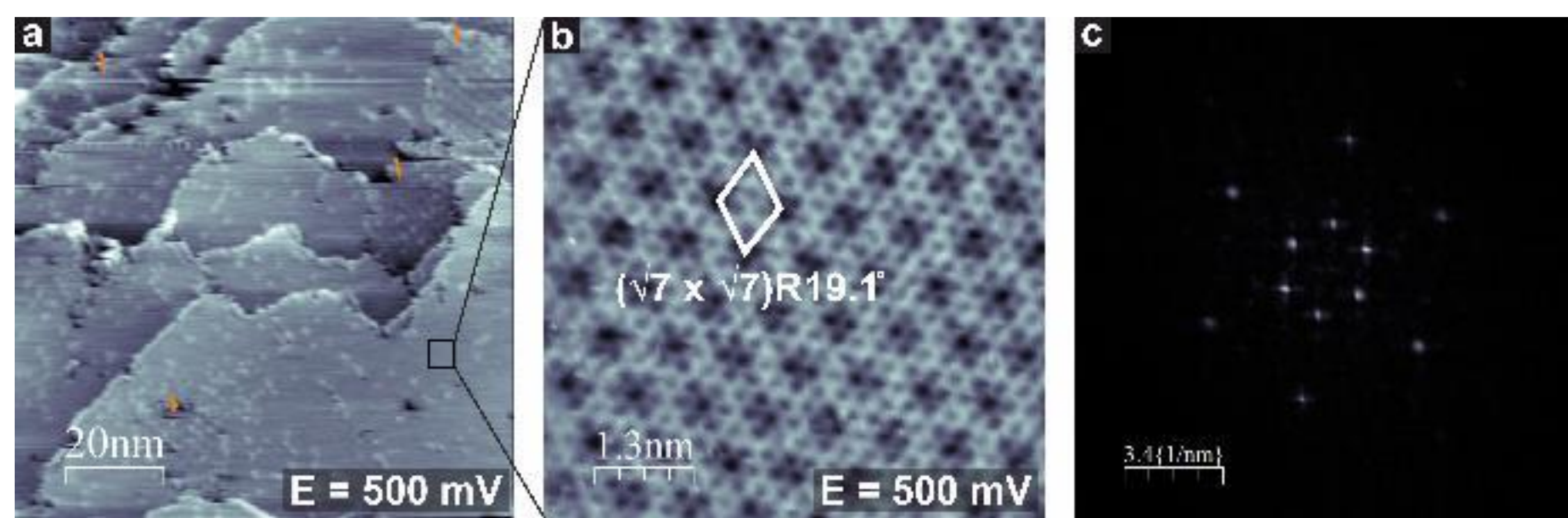
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INTRODUCTION

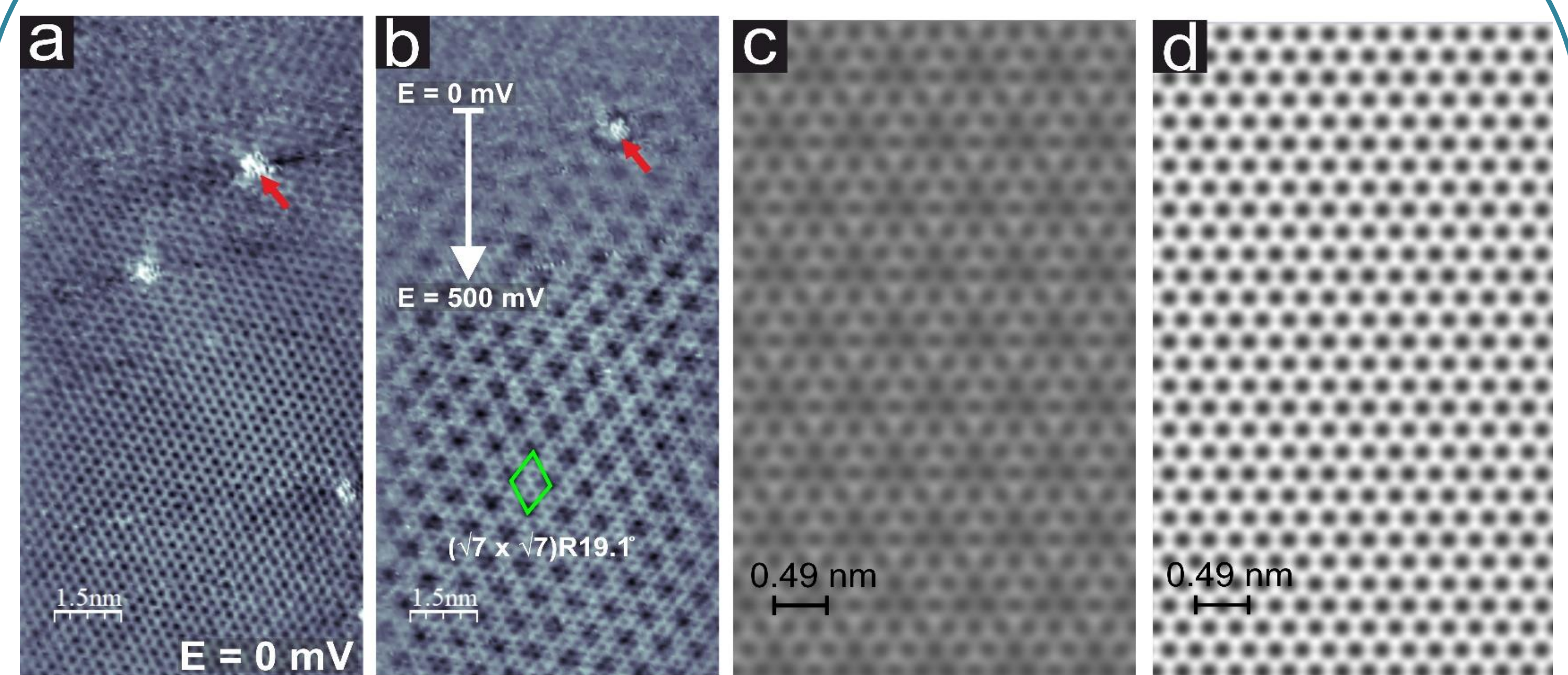
In this work we present a combined experimental and theoretical study of tuning the HER reactivity of the state-of-the-art metallic electrocatalyst platinum (Pt), with graphene (Gr) and iron (Fe). Experimental methods such as electrochemical scanning tunneling microscopy (EC-STM), and cyclic voltammetry are combinedly used to image and probe the reactivity simultaneously during the reaction. Structure and further chemical properties are explored by employing low-energy electron diffraction (LEED) and X-ray photoemission spectroscopy (XPS). Using density functional theory (DFT) the most stable geometries and the HER reactivities of the two systems namely Gr/Pt(111) and Gr/Fe/Pt(111) are determined computationally. In the former the presence of Gr is observed to increase the selectivity/permeability towards protons [1] and at the same time weaken the binding energy of H compared to that on bare Pt [2]. This favors the diffusion of the H atoms at the interface and hence H<sub>2</sub> molecular desorption. The simulated H adsorption energy weakens further in the presence of intercalated Fe at the Gr/Pt(111) interface. Experimentally, a tremendous increase in the HER activity is observed, pointing towards the possibility of replacing the expensive Pt by combining Gr and Fe.

EXPERIMENTAL ELECTROCHEMICAL STM AND LEED

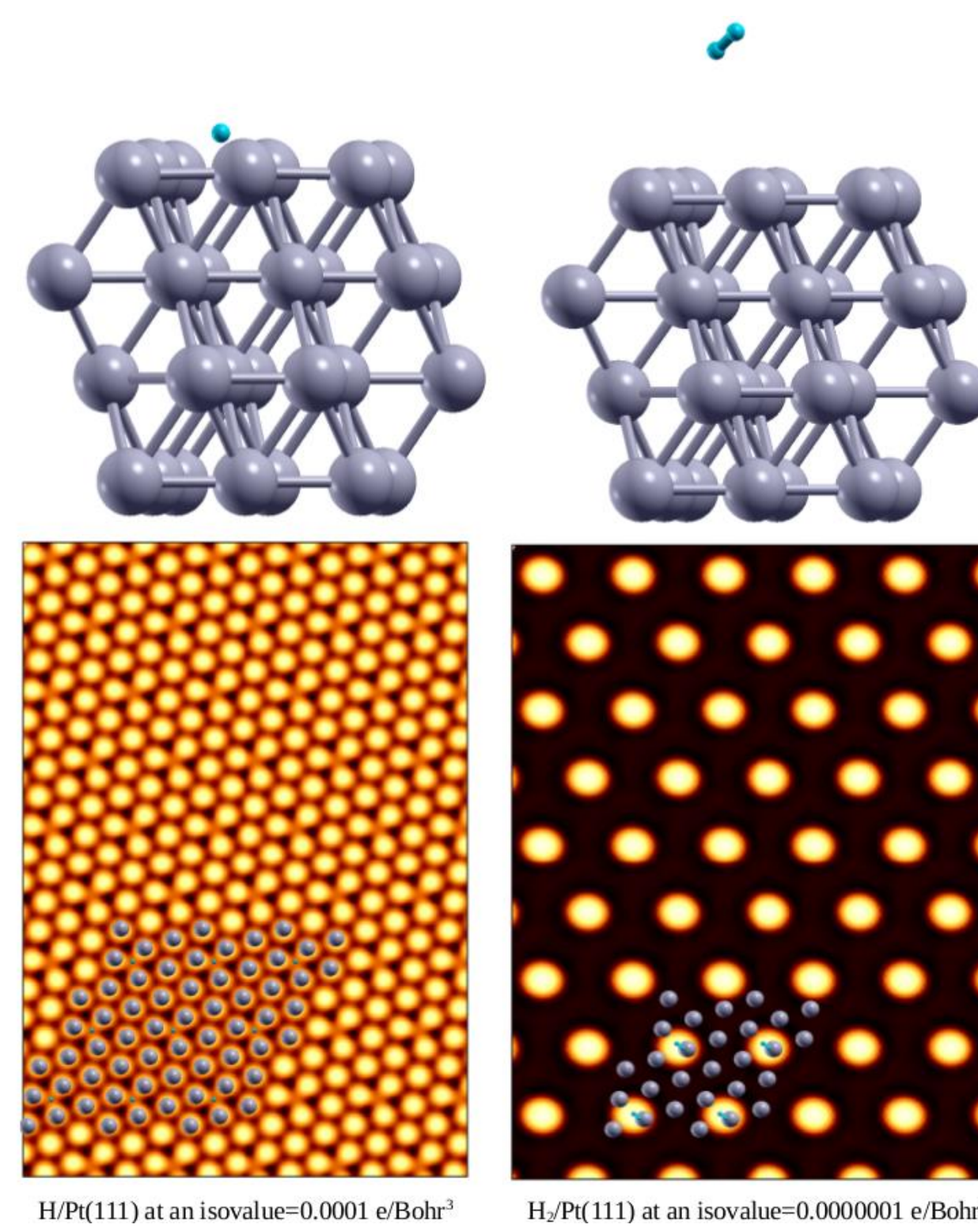


( $\sqrt{7} \times \sqrt{7}$ ) R 19.1° Graphene on Pt(111)

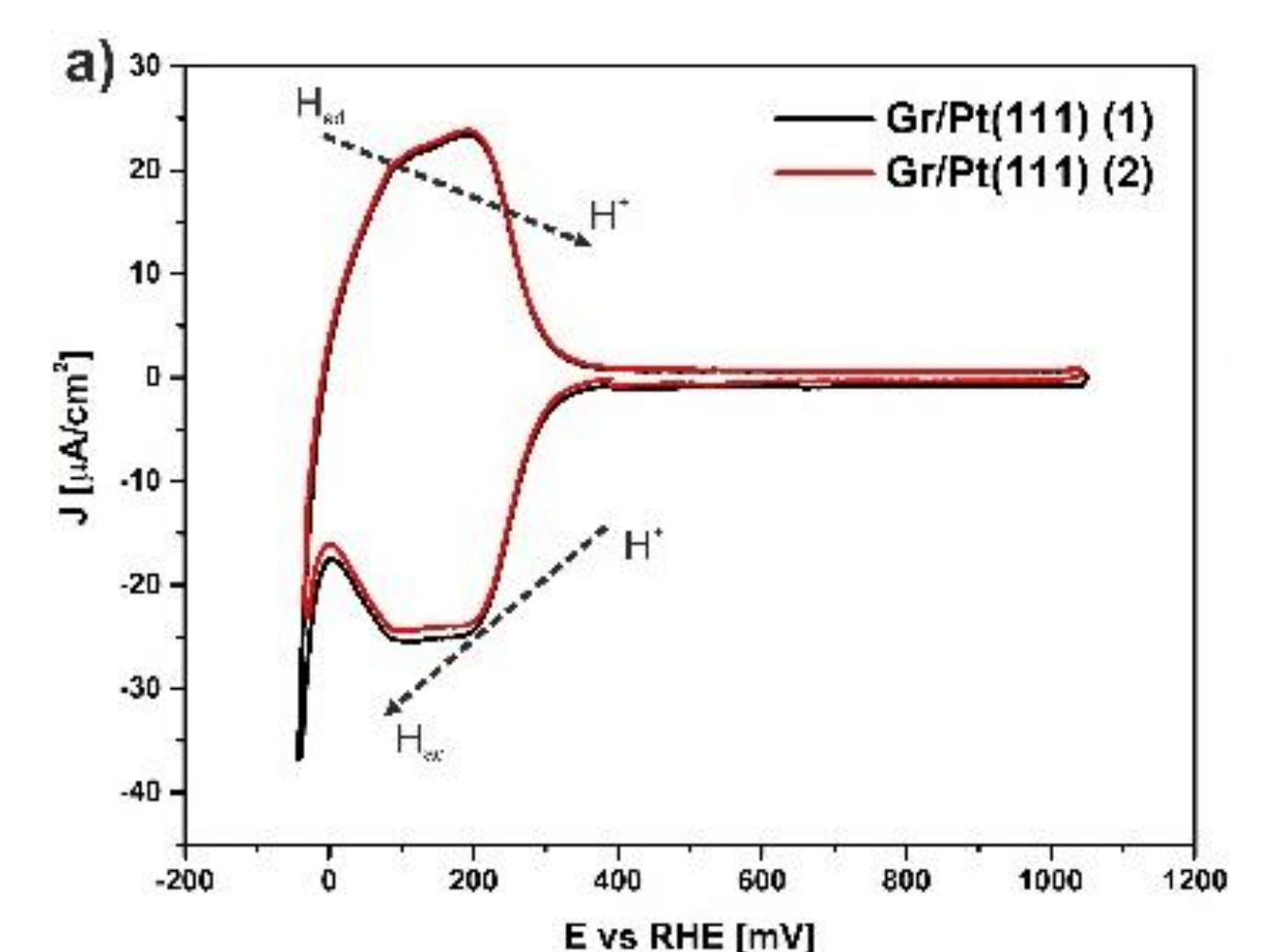
EXPERIMENTAL (a, b) AND SIMULATED (c, d) STM IMAGES OF Gr/Pt(111) DURING HER



Bright spots marked by the red arrows in (a, b) at graphene defects shows H<sub>2</sub> desorption as also in the simulations on Pt(111) shown below:



CYCLIC VOLTAMMETRY (CV)

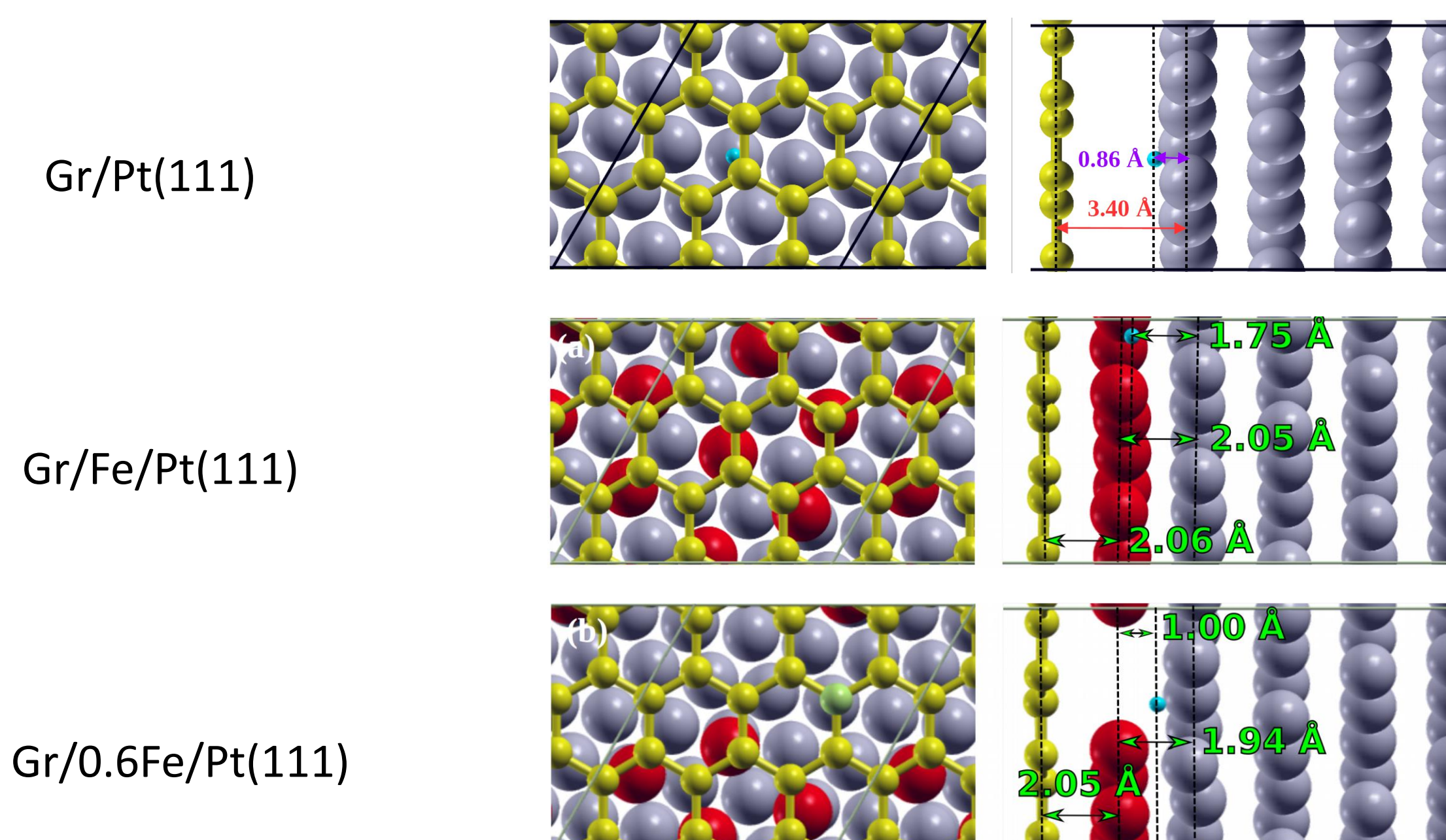


CV of Gr/Pt(111) in O<sub>2</sub> saturated 0.1 M HClO<sub>4</sub>

How to simulate HER?

The Gibb's free energy ( $\Delta G_{H^*}$ ) of atomic hydrogen binding to the surface of the catalyst is the descriptor used to compare the performance of the catalysts towards HER. Firstly the adsorption energy is computed as follows:

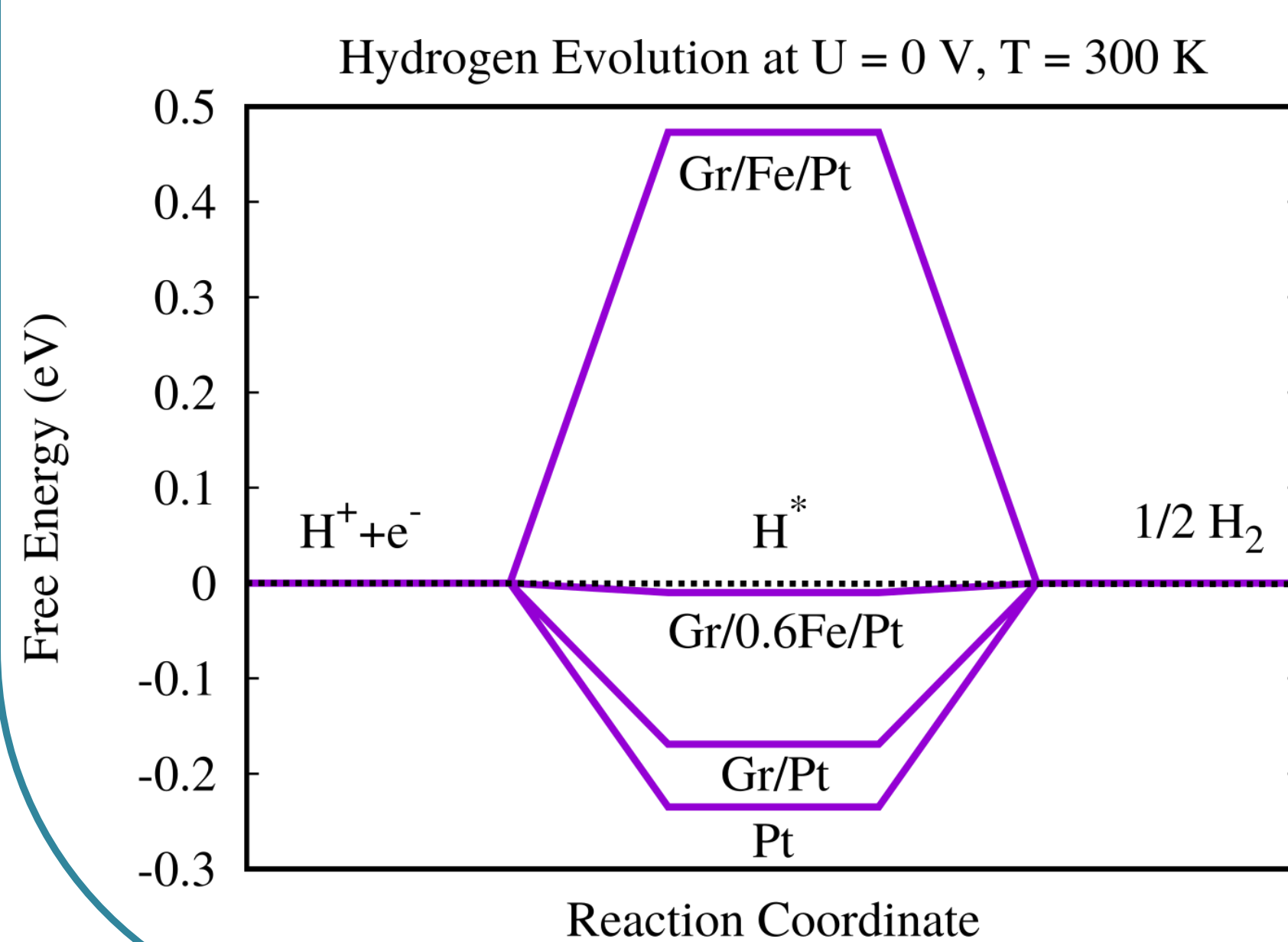
$$\Delta E_{H^*} = (1/n) [E_{(surf+nH)} - E_{(surf)} - n \cdot \frac{1}{2} E_{(H_2(g))}]$$



Followed by the calculation of the Gibb's free energy as:

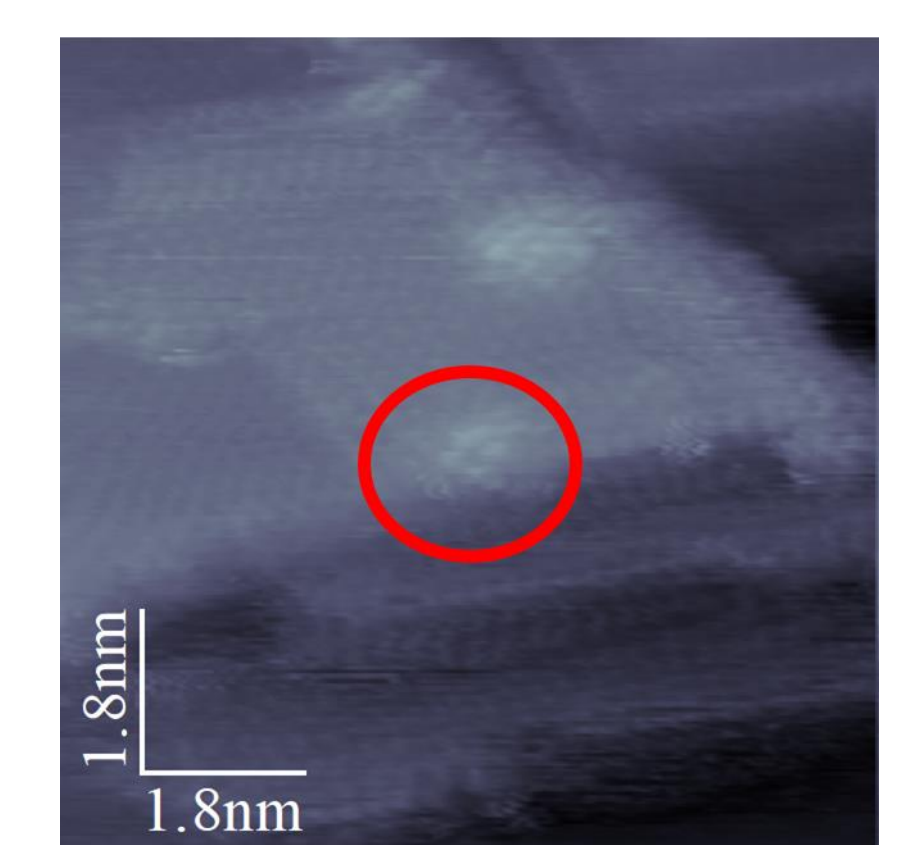
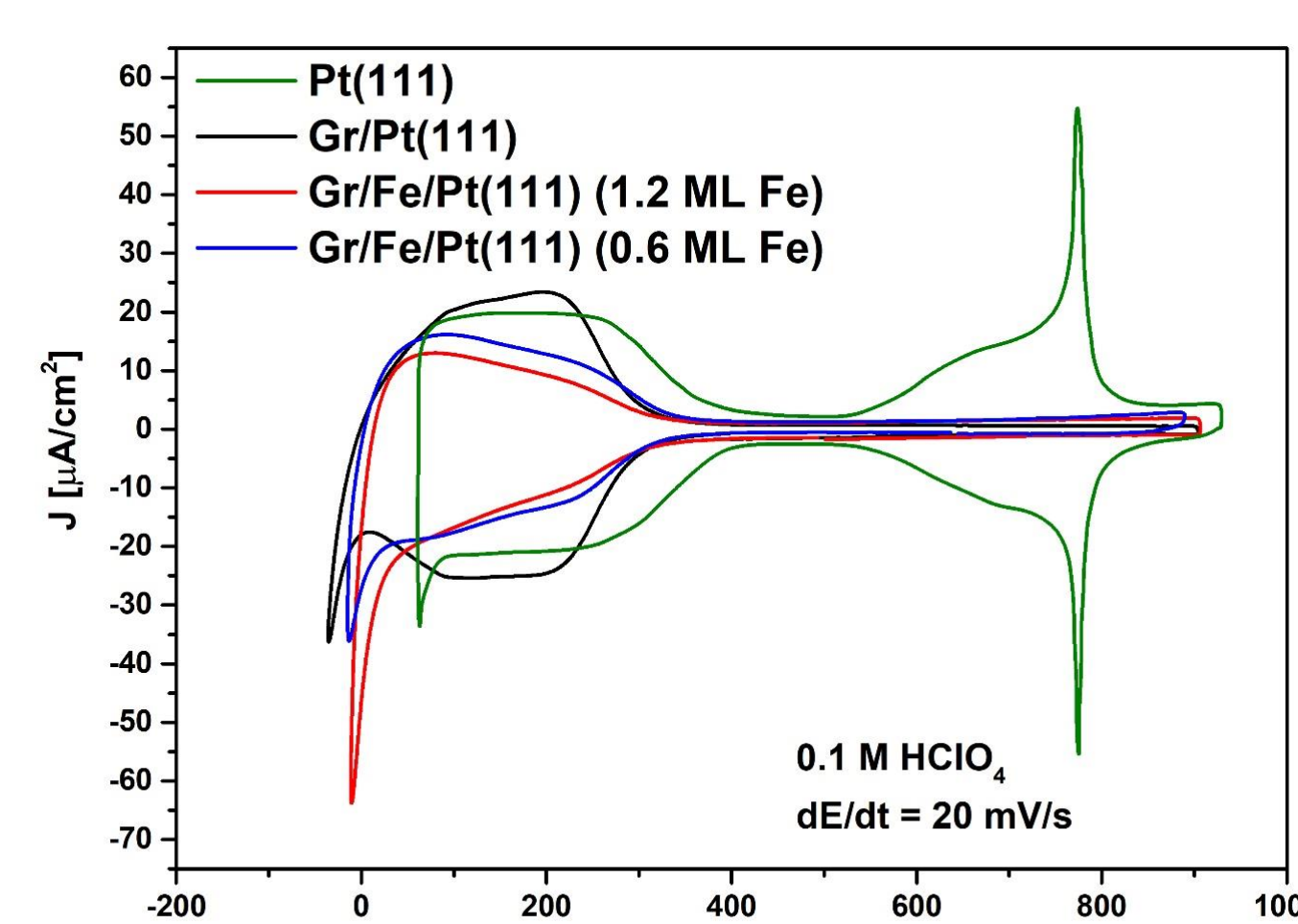
$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE_{H^*} - T\Delta S_{H^*} = \Delta E_{H^*} + 0.21 \text{ eV (by computing vibrational frequencies [3])}$$

According to Sabatier's principle too strong hydrogen binding results in catalyst poisoning and too weak will require higher overpotential. Hence, the ideal value is  $\Delta G_{H^*} = 0 \text{ eV}$ .

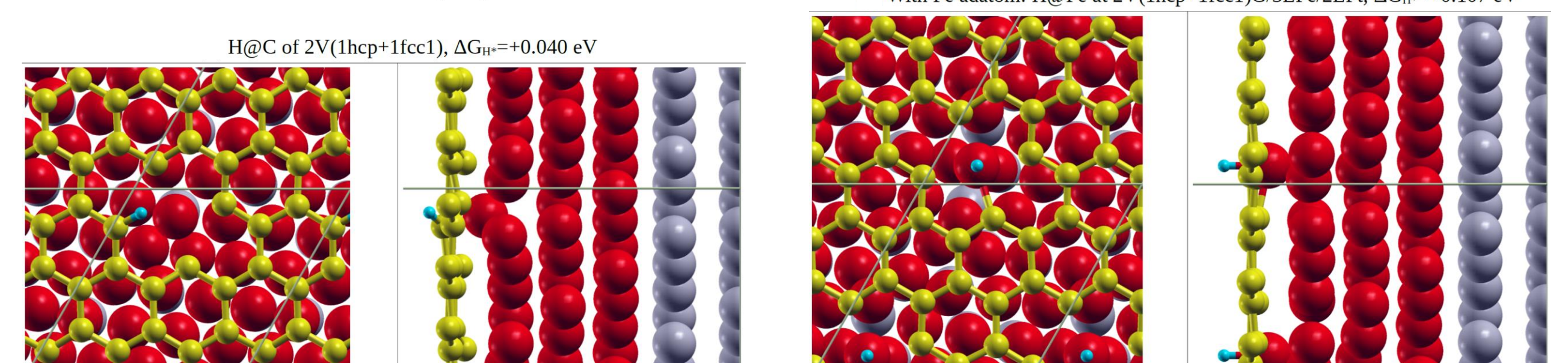


Experimental Q (μC/cm <sup>2</sup> )	
Pt(111)	223
Gr/Pt(111)	222
Gr/Fe(0.6ML)/Pt(111)	123
Gr/Fe(1.2ML)/Pt(111)	80

WHAT HAPPENS WITH MORE Fe?



Gr/(3ML)Fe/Pt STM, E = 75 mV, U<sub>b</sub> = -13 mV, I<sub>t</sub> = -1.6 nA



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REFERENCES

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- [2] Y. Zhou, W. Chen, P. Cui, J. Zeng, Z. Lin, E. Kaxiras, Z. Zhang. Nano Lett., 16, (2016), 6058.
- [3] Atkins, P. W., Physical Chemistry, 6th ed.; Oxford University Press: Oxford, UK, 1998; p 582.