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Monitoring Active Sites for Hydrogen Evolution Reaction at Model Carbon Surfaces

Supplementary Information

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Contents

S1. STM recorded in air

Scanning tunneling microscopy (STM) recorded in air was performed to visualize the surface. **Figure S1**a shows a large-scale image where both basal and edge planes can be observed. Here, one can see edge planes as sharp lines dividing adjacent basal planes from each other. An example of the height profile (line scan) across several steps is given in the inset and marked by a black line in the STM image. By decreasing the scan size further, the typical honeycomb lattice of graphite can be resolved, as is shown in **Figure S1**b. For better understanding, basal and edge planes are marked in the inset of **Figure S1**b.

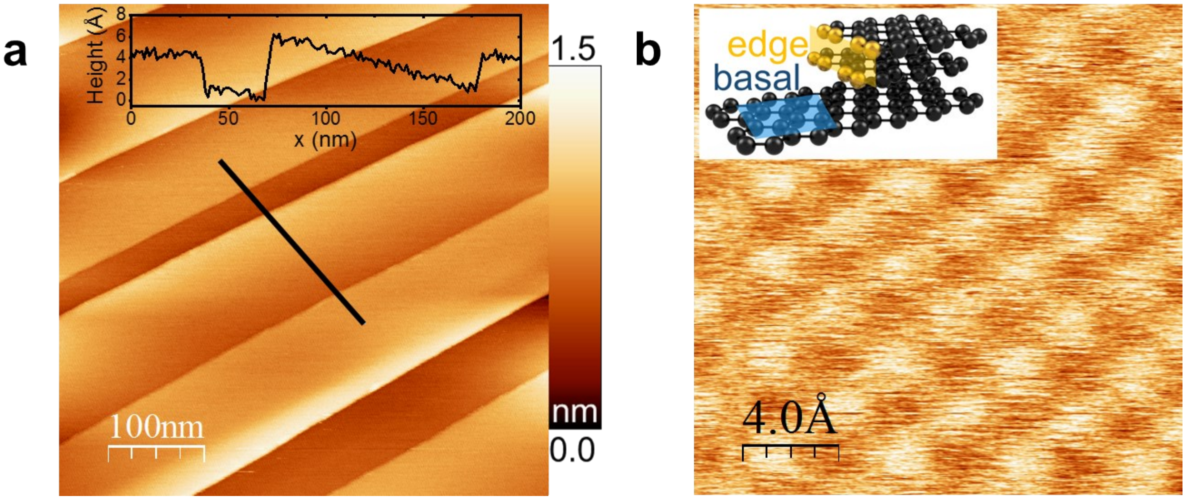

Figure S1. STM images of the HOPG sample recorded in air. **a,** Large-scale STM image of HOPG showing multiple basal and edge planes. The latter can be observed as sharp lines. An exemplary line scan across the step edges is given in the inset. The position of the line scan is given by the black line in the main image. **b,** High-resolution image of a basal plane showing the typical honeycomb lattice of HOPG. The sketch in the inset illustrates the difference between basal and edge planes.

S2. Further explanation about the n-EC-STM technique

As already stated in the main text, in EC-STM, the sample potential can be adjusted such that a reaction takes place (‘on’) or not (‘off’). If the reaction is switched ‘on’, the structure and composition of the electrolyte in the tunneling gap will continuously change. This instant is illustrated in **Figure S2** taking the example of the oxygen evolution reaction (OER). However, the same considerations hold for the HER as well. In **Figure S2**, the electrolyte is simplified to pure water. In the unperturbed state (a), the water molecules are perfectly aligned to the electrode surface by hydrogen bonds. An ongoing reaction involves multiple charge transfers at the electrode-electrolyte interface (b-c) as well as the evolution of the reaction product (f-i). During the reaction, the water molecules in the tunneling gap are persistently forced to re-arrange.

The influence of a change in tunneling medium on the STM signal should be accounted for by a short literature review. Already in the early days of ultrahigh-vacuum STM, it has been found that the diffusion of atoms along the surface which eventually cross the tunneling region, lead to changes in the tunneling current. These changes can either result in current pulses, i.e., an abrupt increase of the tunneling current over orders of magnitude[1], or an increase in the noise level of the current.[2] Later on, when performing STM in solution, it was stated that the tunneling current does not simply depend exponentially on the tunneling barrier, but that this behavior is modulated by the structure of the (water) molecules within the tunneling gap.[3] Additional studies confirmed that the presence of ions near the solid/liquid interface influences the tunneling current.[4] With these studies in mind, it is comprehensible why the noise level of the STM signal is increased when a reaction is ongoing. An ongoing reaction will change the composition and structure of the electrolyte as explained above. These subsequent changes in the STM signal are, thus, the most pronounced if the tip is placed over an active site.

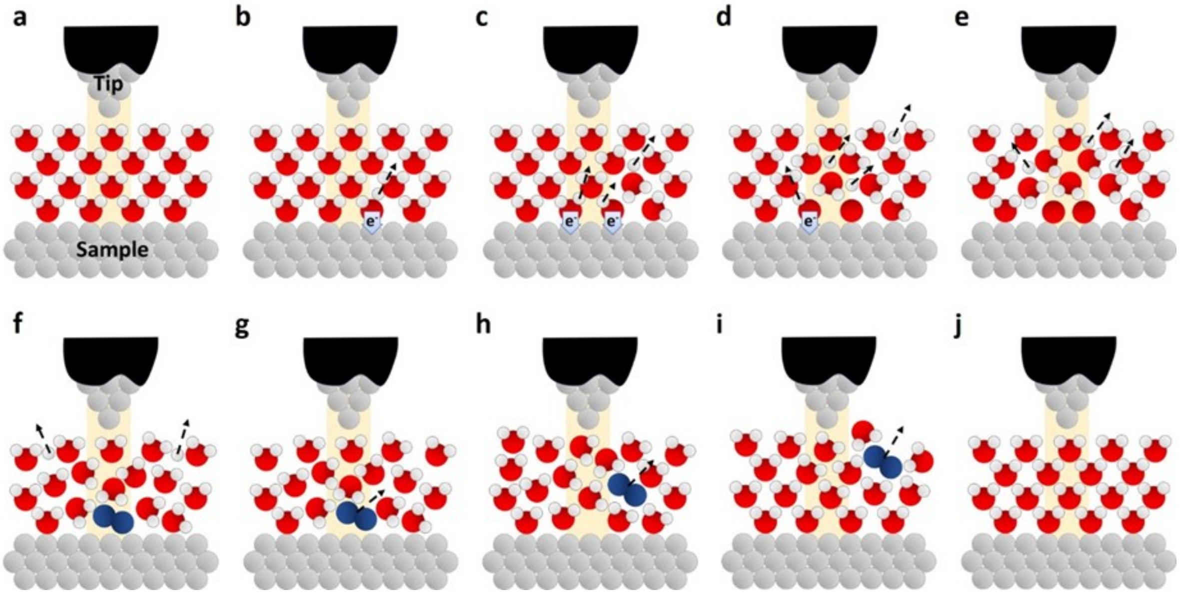

Figure S2. Simplified illustration of the oxygen evolution at the sample-electrolyte interface. The electrolyte is simplified to pure water, showing a perfectly aligned hydrogen bonded network when unperturbed. Due to the reaction, some of the hydrogen bonds are forced to be broken and the formally regular network of water molecules is forced to rearrange. Reprinted with permission[i] from reference 5. Copyright Wiley-VCH GmbH, 2020.

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S3. Additional STM images

Figure S3 shows additional electrochemical scanning tunneling microscopy under reaction conditions (n-EC-STM) images on HOPG. In each subimage, the potential is set such that the HER takes place ('on'). In **Figure S3**a distinct spots of brighter color can be observed along the step edge. They show a higher intensity of the STM signal than sites at the adjacent terrace, from which can be deduced that they constitute active sites. Below the image, two exemplary line scans across the step edge are given. One is including an active site (red), the other one is including less active sites (black). A clear intensity maximum of the STM signal can be observed at the step edge for the red line scan. **Figure S3**b shows a defective part of the surface. Again, the active sites of highest intensity lay near the defect sites, whereas the defect-free terrace shows atoms of less intense and homogeneous STM signal. **Figure S3**c shows the high resolution image of a step edge. In the corresponding image processed by fast Fourier transformation (FFT), given in **Figure S3**d, distinct active sites near the step edge can be observed. Line scans are given including an active site (red) and only inactive sites (black).

Figure S4 shows the original n-EC-STM images given in the main text as Figure 4, prior to FFT.

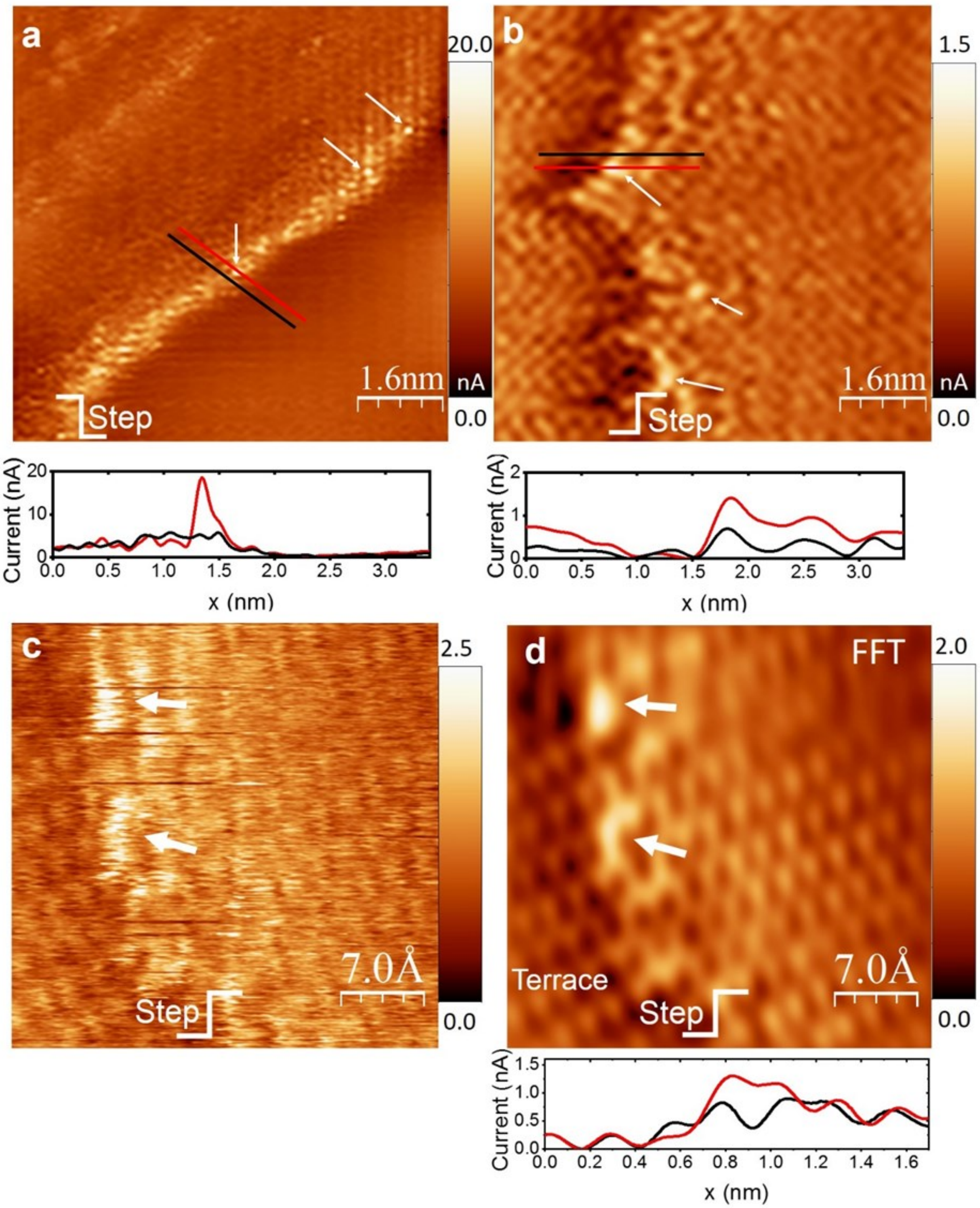


Figure S3. Additional high-resolution images in acidic medium with HER ‘on’. a, and c, show active sites near terraces, b, shows active sites along a defective stepped region. d, is the corresponding FFT image of c).

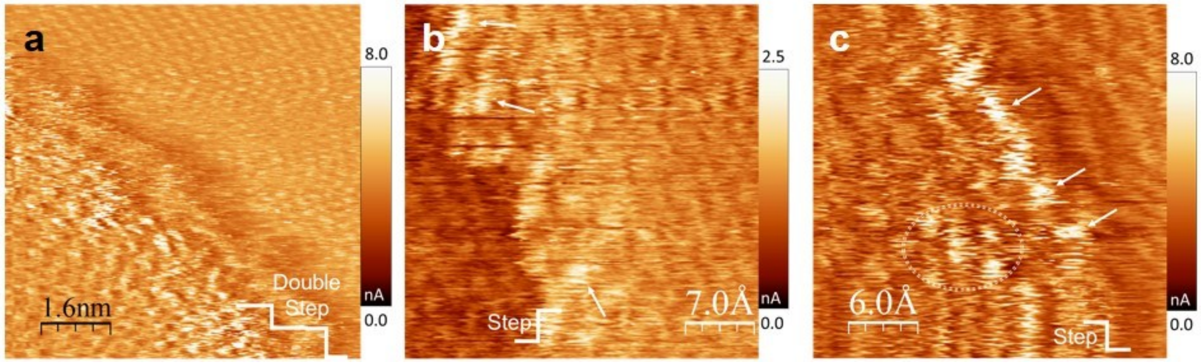


Figure S4. As-recorded n-EC-STM images with high resolution. Corresponding FFT images are shown and discussed in main text, Figure 4.

Table S1. Experimental parameters of n-EC-STM images.

	Tip Potential (mV_{Pt})	Current Setpoint (nA)
Figure 3	-225	3
Figure 4a	-600	2
Figure 4b	-225	4
Figure 4c	-600	6
Figure S3a	-600	2
Figure S3b	-450	2
Figure S3c	-600	6

S4. Additional computational details

The following figures show the location of the active sites on cell$_1$ and cell$_2$. In **Figure S5**-**Figure S11**, C1 and C2 stand for cell$_1$ and cell$_2$, D stands for carbon divacancy, SE stands for a layer containing step edges, P stands for pristine. In Figures S4-S9, 2×2 repetitions of the respective unit cells are shown.

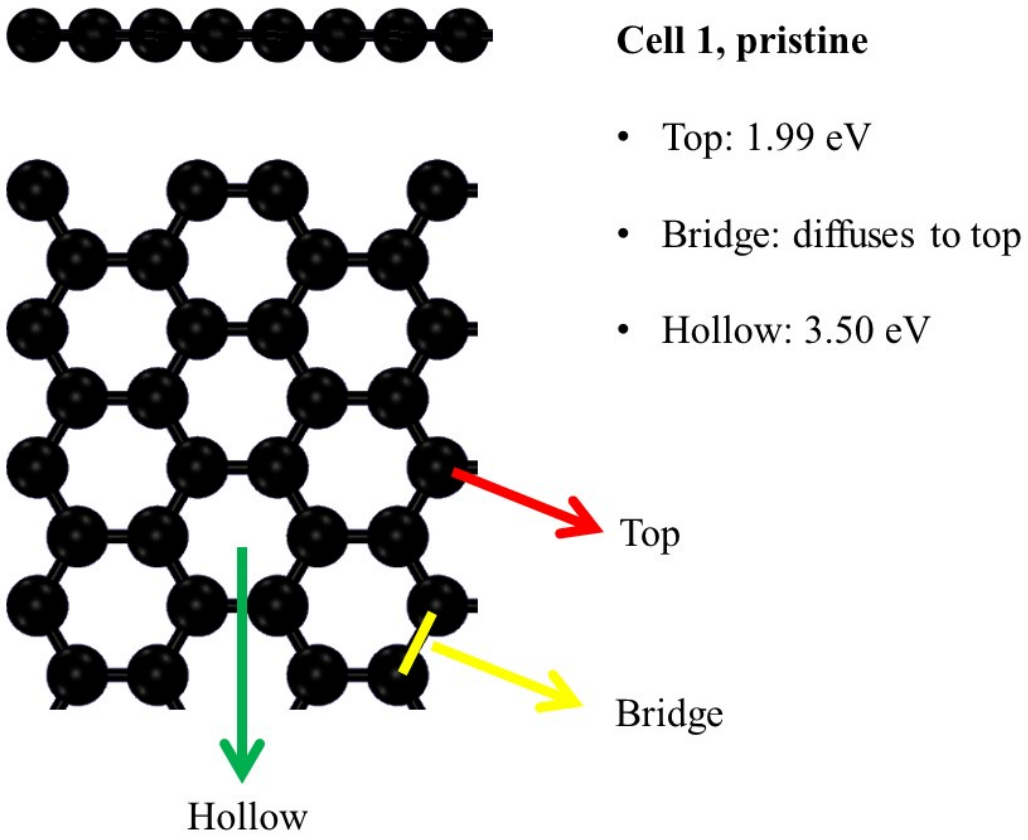
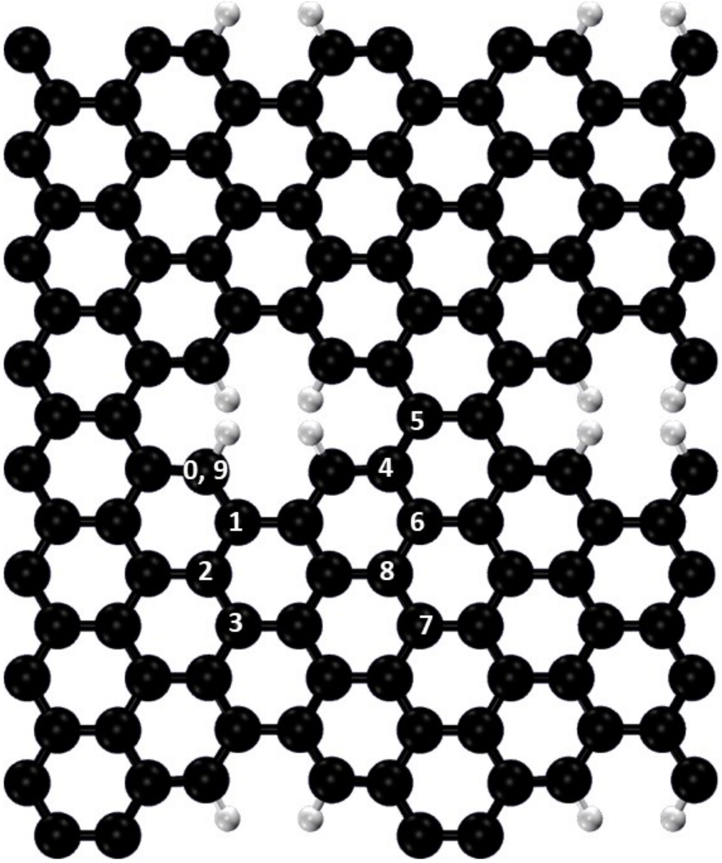


Figure S5. Active sites on pristine graphene and the corresponding free energies of adsorption of hydrogen**.**



Cell 1, C divacancy

- C1-D-0: -1.82 eV
- C1-D-1: 1.68 eV
- C1-D-2: 2.55 eV
- C1-D-3: 1.76 eV
- C1-D-4: 1.75 eV
- C1-D-5: 1.54 eV
- C1-D-6: 2.77 eV
- C1-D-7: 1.92 eV
- C1-D-8: 1.99 eV
- C1-D-9: 0.88 eV

Figure S6. Active sites near a C divacancy on cell$_1$ and the corresponding free energies of adsorption of hydrogen. C1-D-0: adsorption site for a passivating H atom. C1-D-9: Adsorption site with a passivating H atom in place.

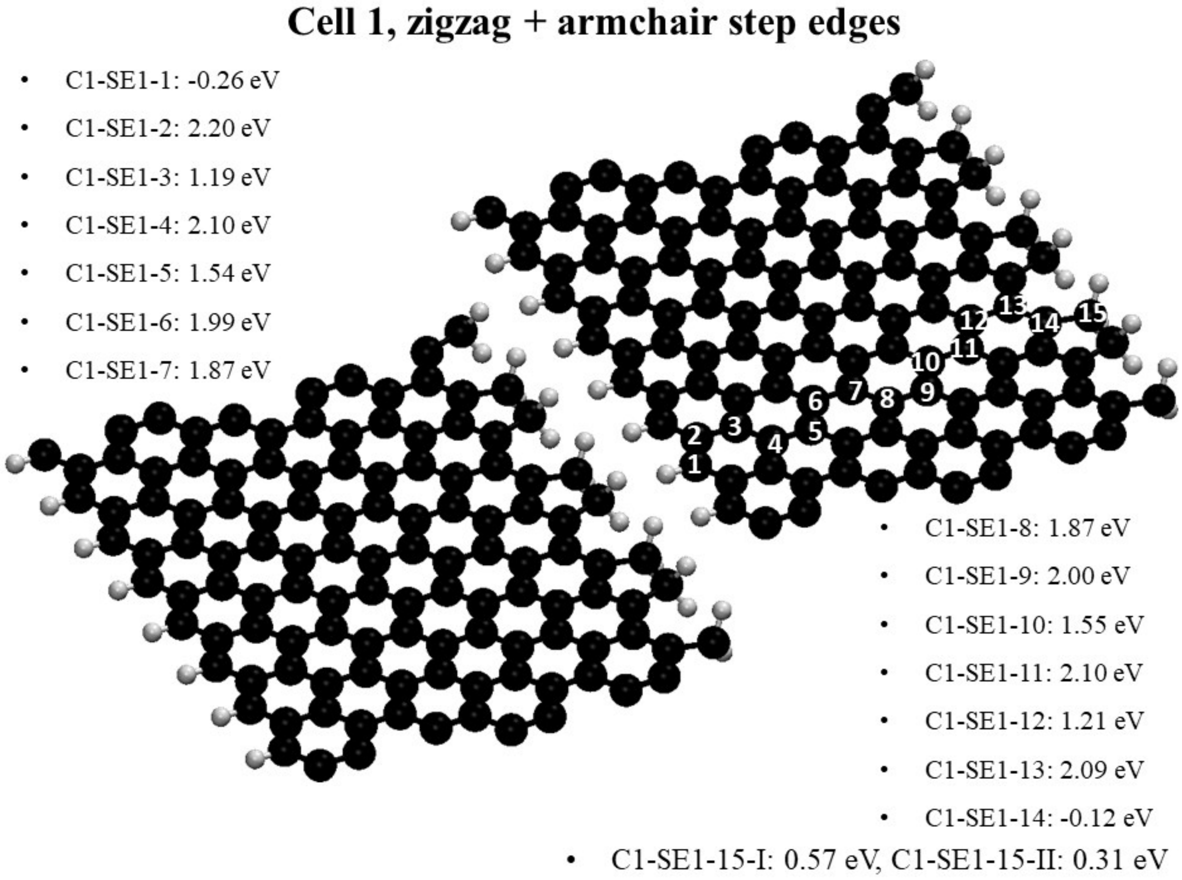


Figure S7. Active sites at a graphene layer with step edges 1 on cell_1 and their corresponding free energies of adsorption of hydrogen.

Cell 1, armchair + armchair step edges

- C1-SE2-1: 1.34 eV
- C1-SE2-2: 1.86eV
- C1-SE2-3: 2.10 eV
- C1-SE2-4: 1.86 eV

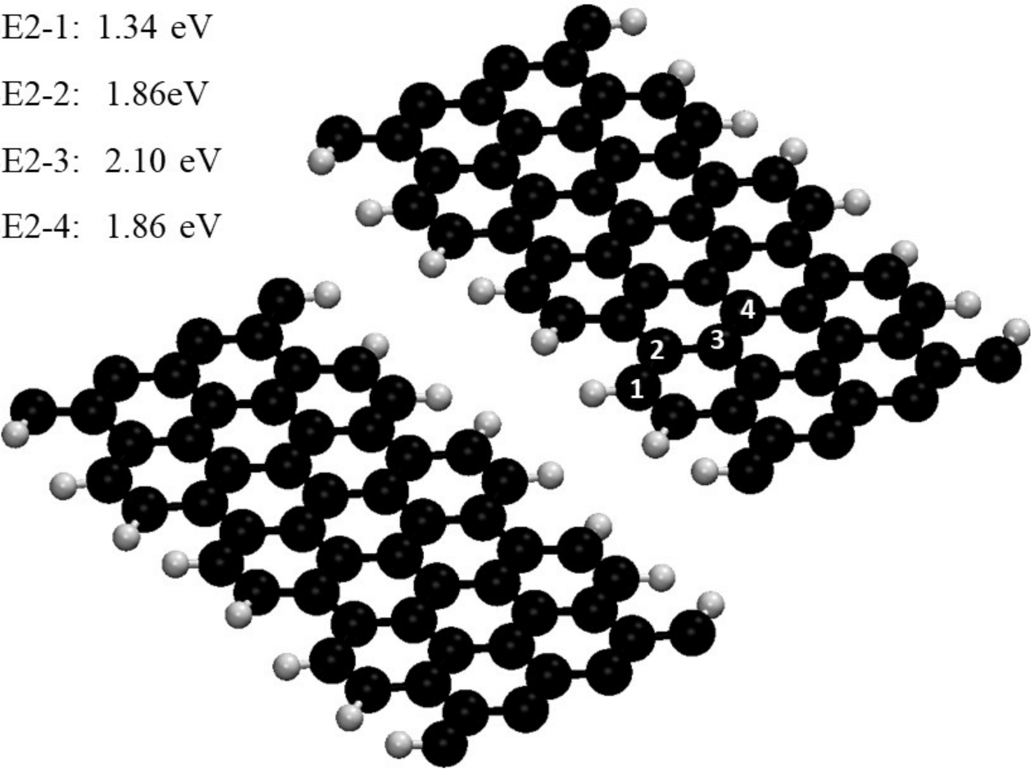
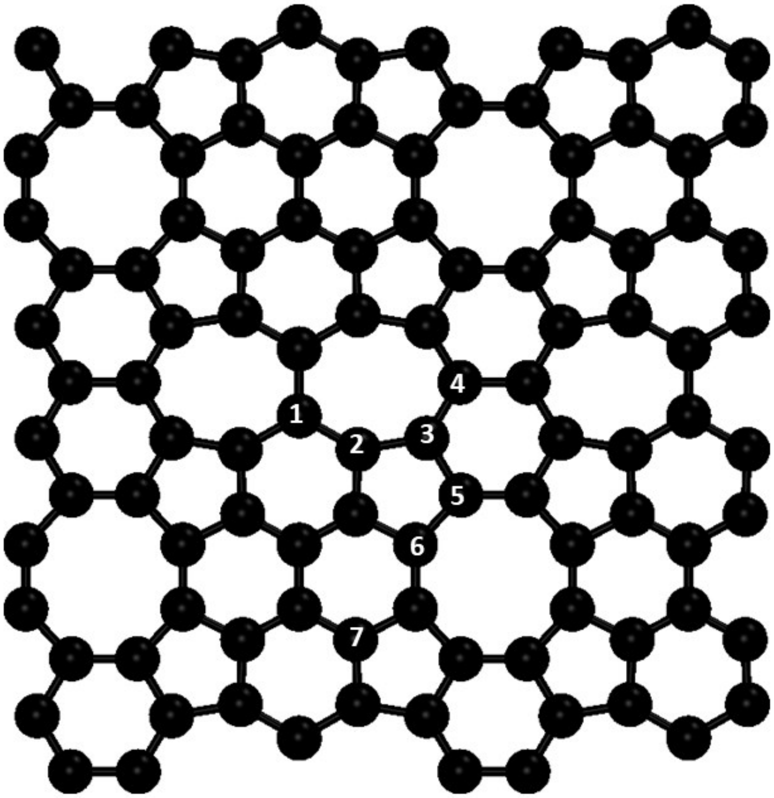


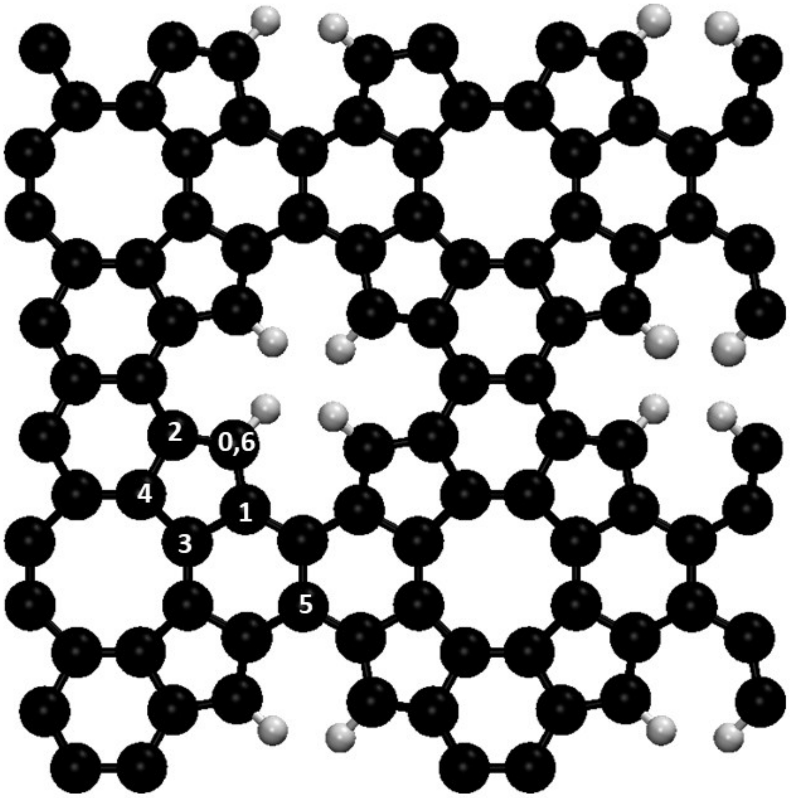
Figure S8. Active sites at a graphene layer with step edges 2 on cell1 and their corresponding free energies of adsorption of hydrogen.



Cell 2, pristine

- C2-P-1: 1.01 eV
- C2-P-2: 0.90 eV
- C2-P-3: 0.70 eV
- C2-P-4: 1.27 eV
- C2-P-5: 0.91 eV
- C2-P-6: 0.76 eV
- C2-P-7: 1.36 eV

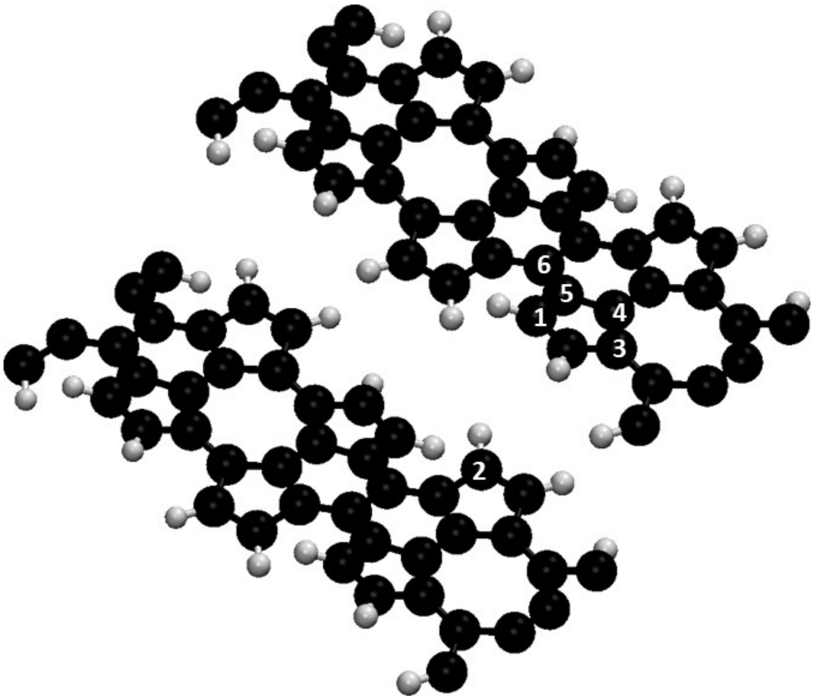
Figure S9. Active sites at a defective graphene layer without C vacancies on cell$_2$ and their corresponding free energies of adsorption of hydrogen.



Cell 2, C divacancy

- C2-D-0: -1.81 eV
- C2-D-1: 0.41 eV
- C2-D-2: 0.80 eV
- C2-D-3: 0.64 eV
- C2-D-4: 0.63 eV
- C2-D-5: 0.62 eV
- C2-D-6: -0.24 eV

Figure S10. Active sites near a C divacancy on cell$_2$ and the corresponding free energies of adsorption of hydrogen. C2-D-0: adsorption site for a passivating H atom. C1-D-6: Adsorption site with a passivating H atom in place.



Cell 2, step edges

C2-SE-1: 1.53 eV

C2-SE-2: 1.53 eV

C2-SE-3: 2.25 eV

C2-SE-4: 0.74 eV

C2-SE-5: 1.92 eV

C2-SE-6: 2.33 eV

Figure S11. Active sites at a graphene layer with step edges on cell$_2$ and their corresponding free energies of adsorption of hydrogen.

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