Supplementary Information

Graphene flakes from local electroexfoliation of graphite with a STM tip*

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S1. Molecular dynamics simulations set up

An example of the molecular dynamics simulation set up is shown in figure S1, which consists of a 10 nm x 10 nm graphite surface with a monolayer step ending either on an armchair or a zigzag configuration. We have performed simulations where an upward force is applied at the border of the step, in a radius of 0.5 nm, to mimic the force induced by the applied voltage in the STM experiment, and simulations where the force is applied perpendicular to the step and parallel to the surface, to reproduce the conditions during the scanning of the surface.

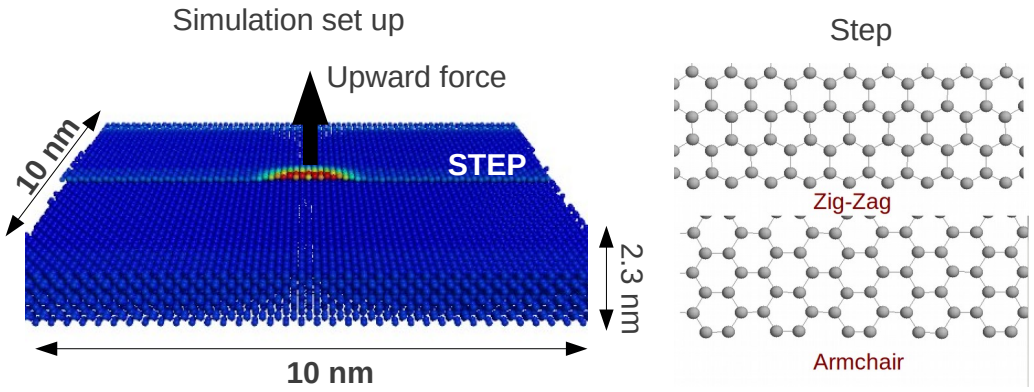

Figure S1: Example of the set up of our molecular dynamics simulations. A monolayer step ending in zigzag or armchair configurations and an upward force (or force parallel to the surface and perpendicular to the step in other simulations) in a radius of 0.5 nm at the edge of the terrace.

* Electronic supplementary information (ESI) available

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S2. STM images of nanostructures formed on graphite surfaces

Increasing the voltage applied between tip and sample for a constant current it is possible to form different nanostructures on the graphite surface. Figure S2 shows the partial tear of two different terraces of graphite, before (left) and after (right) applying a voltage ramp.

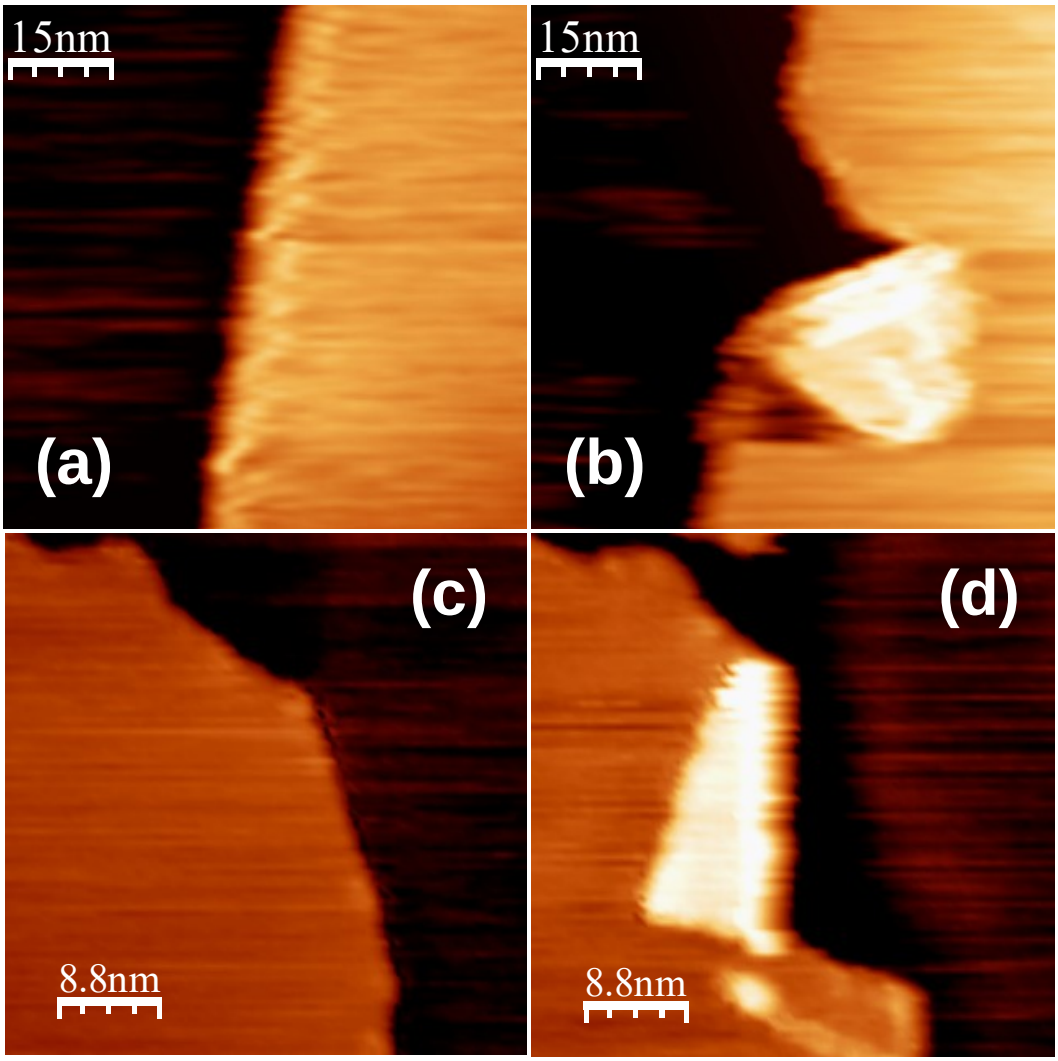

Figure S2: Creating defects in HOPG terraces. On the left (a and c), initial image of graphite terraces. On the right (b and d), after applying a voltage ramp we observe the tearing of the terraces.

A second example is shown in Figure S3. In this case we show a terrace, which has been modified at several places.

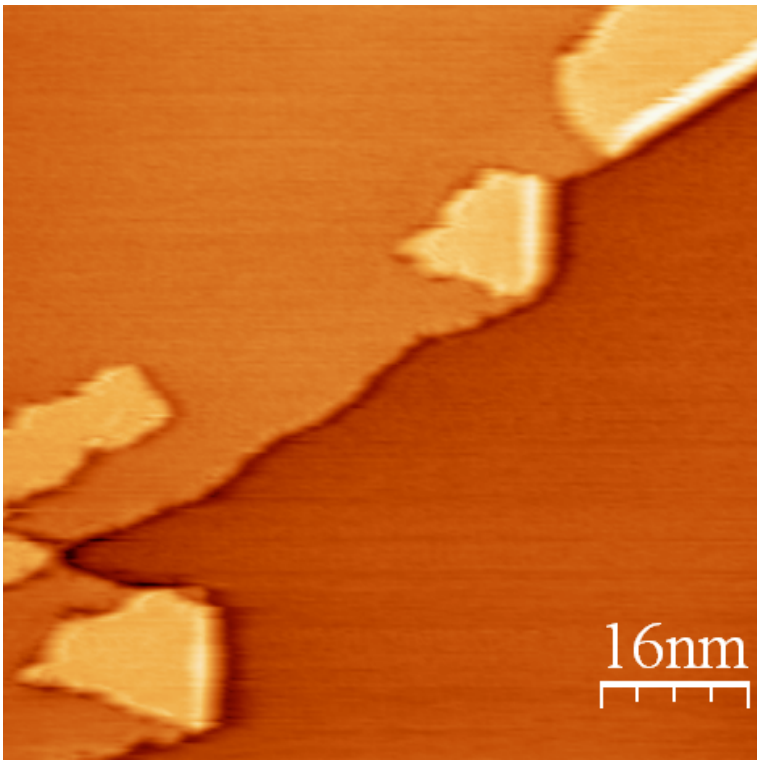

Figure S3: Different modifications on a graphite terrace.

Figure S4 shows the folding of the terrace together with the evolution of the tip with the applied voltage. The voltage ramp detaches the grahene layer and the tip retracts about 1 nm (voltages between 3-5 V), then the tip retracts very abruptly when the applied voltage is ~ 5 V. The tip retracts ~ 4 nm during the voltage ramp while the final flake is about 11 nm wide (Figure S4(b)).

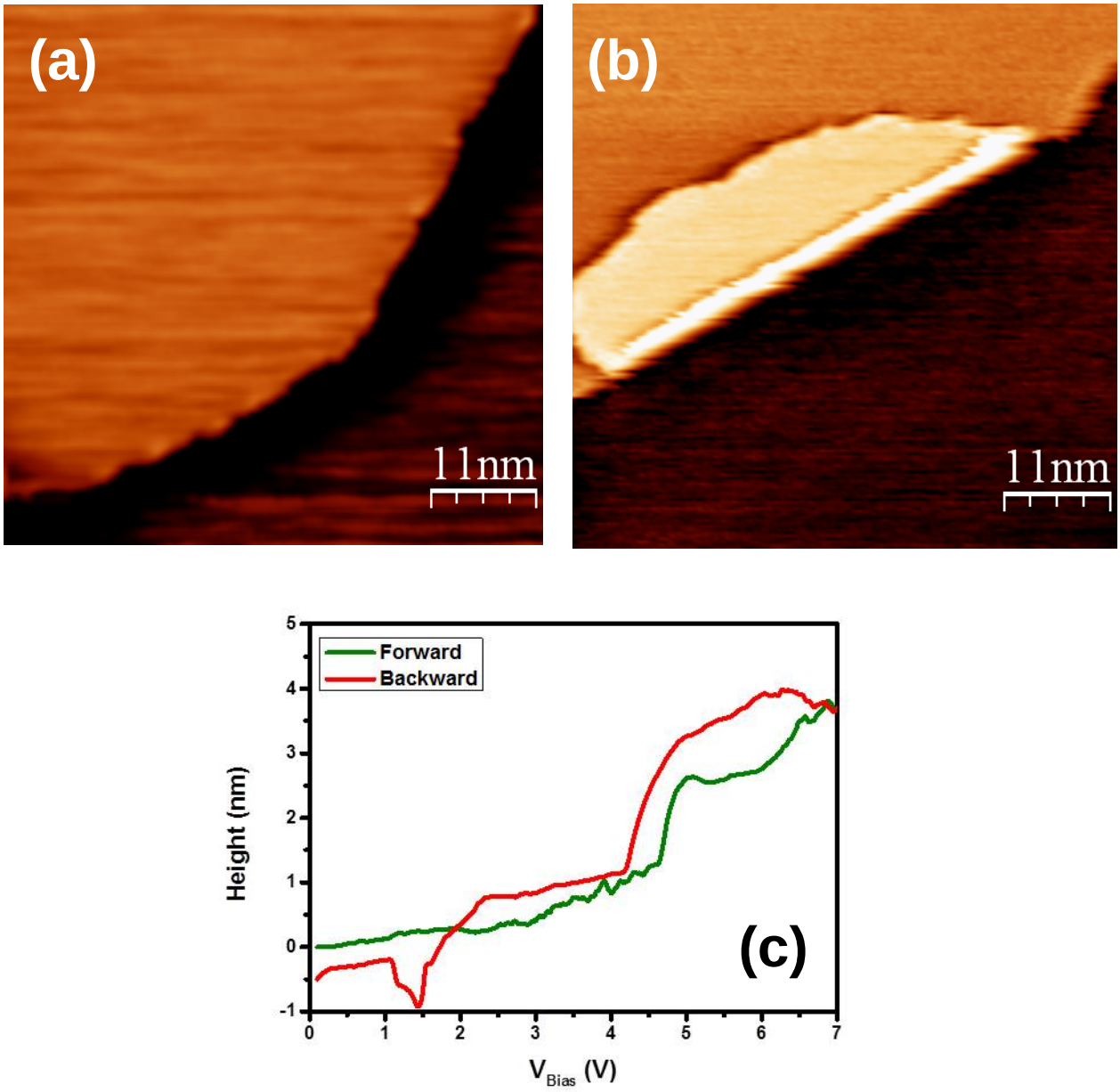

Figure S4: The two first panels show a terrace before (a) and after (b) being folded. The evolution of the tip-height while the voltage is increased is shown on the last panel (c).

The last example in Figure S5, shows the evolution of the tip during a voltage ramp. This corresponds to the case presented in Figure 2 of the manuscript, where first a defect is produced and the layer is slightly lifted. This figure shows that the tip only retracts ~ 1 nm.

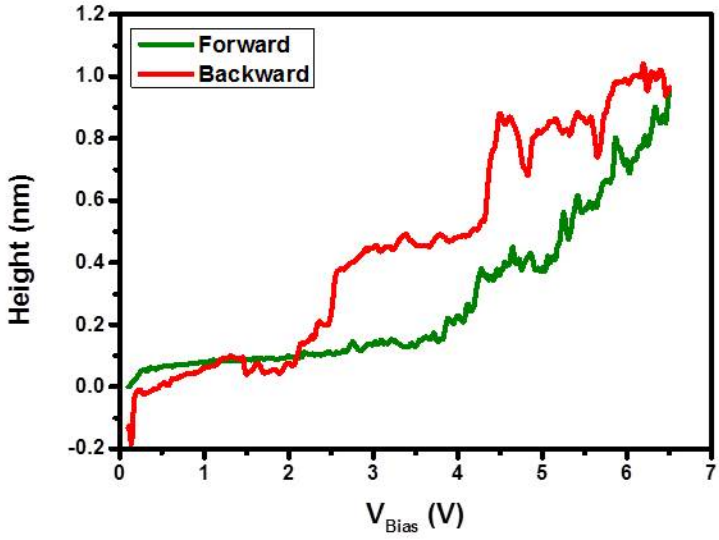

Figure S5: Evolution of the tip-height while the voltage is increased for the case of Figure 2.

S3. Molecular dynamics simulations of lifting of a graphite layer

Figure S6 shows the process of lifting and breaking a layer of graphite with a zigzag edge terrace. If the force is high enough, like in the case shown in figure S6, the graphite layer is torn close to the location of the applied force (see figures S6(b, c)). Even after removing the force, the graphene layer continues breaking apart (figures S6 (d, e)) until it stops and relaxes, folding over itself (figure S6(f)). A movie of this simulation can be seen at Video S1. In most of the cases studied, tearing occurs not only close to where the force is applied, but also at the edges of the simulation box, where the layers are fixed. If the force is slightly lower, tearing occurs only at the edges, similarly to the simulations of Sen et al. [1]. If the force is lowered even further the layer is only slightly lifted.

Simulations show the formation of triangular flakes, similar to those observed experimentally although at a smaller scale, as presented in the top view of figure S6(f). In this case the layer is lifted several nanometers before tearing and breaking (in the case presented in figure S6 it is lifted about 4 nm). Applying the force for shorter times, it is possible to lift the layer only 1 or 2 nm. When the layer relaxes back, small defects can be observed at the edge of the terrace.

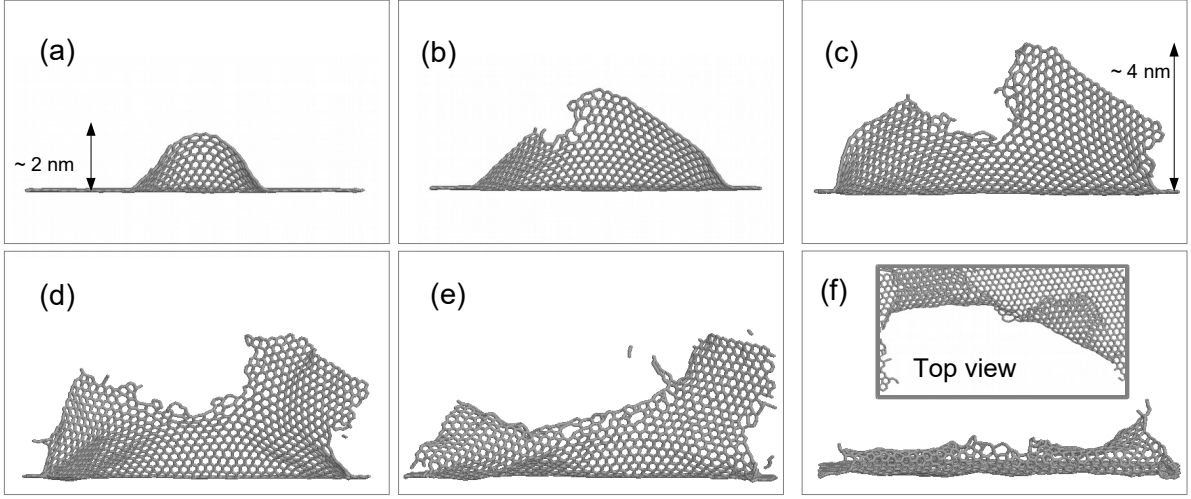

Figure S6: Formation of flakes in a zigzag edge configuration applying an upward force of 2.2 nN/atom in a 0.5 nm radius. Only the top layer of the graphite system is shown. First the layer is lifted up without breaking (a), then defects are formed at the edge, close to where the force is applied (b) and the layer keeps breaking apart (c, d) eventually relaxing (e) and folding back on itself (f) leaving the formation of a triangular flake (top view in (f)). Note that the layer is lifted up to 4 nm before falling back and forming the flake.

Video Captions:

Video S1: Atomistic simulation of an upward force applied perpendicular to the graphite surface near the step edge. The edge in this case ends in a zigzag configuration. A 2.2 nN/atom force is applied in a 0.5 nm radius. This movie shows a side view of the last layer in the graphene sample.

Video S2: Atomistic simulation of a force applied parallel to the graphite surface and perpendicular to the step. The edge in this case ends in an armchair configuration. A 1.9 nN/atom force is applied in a 0.5 nm radius. A small defect at the edge of the step is created initially. The force is applied next to this initial defect. This movie shows a top view of the last layer in the graphene sample. As the layer is being pulled, it tears along the location of the defect.

References

1. Sen, D., Novoselov, K., Reis, P. M. & Buehler, M. J. Tearing of graphene sheets from adhesive substrates produces tapered nanoribbons. *Small* **6,** 1108 (2010).