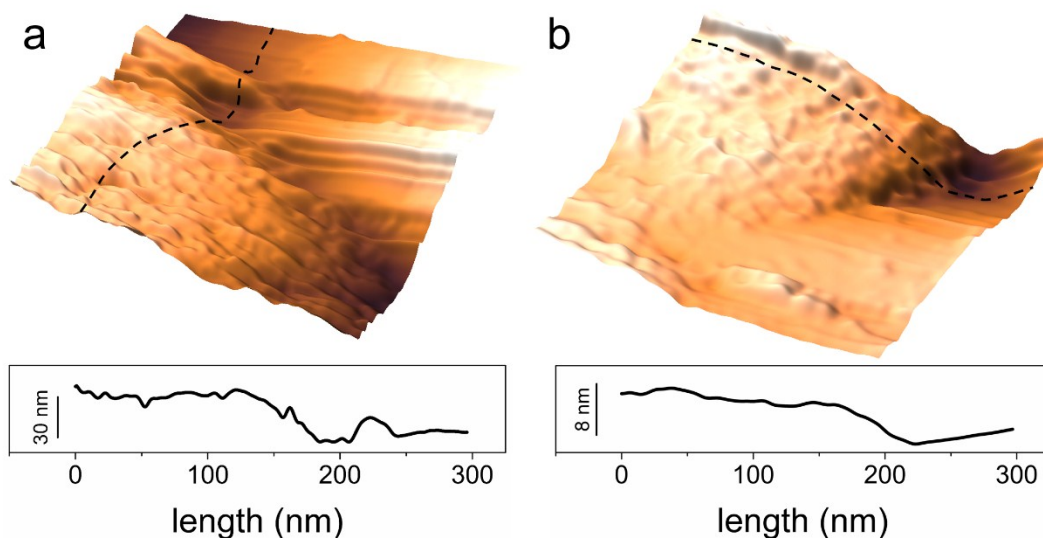


## Supplementary Information

### a) Comparison of surface blistering by using different voltammetry strategies and techniques.

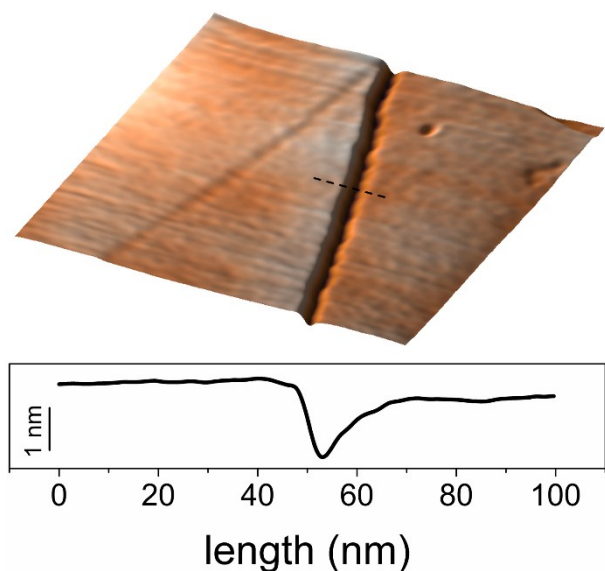
In Figure 2 of the main text, we report the blister formation observed on graphite when consecutive pulses ( $16 \times 0.2 \text{ s} = 3.2 \text{ s}$ ) are applied to the WE. Blisters are also found affecting HOPG if a single long pulse of 3.2 s is applied (see **Figure S1a**), suggesting that the overall time spent at 1.2 V plays a crucial role in surface swelling, instead of the specific sequence of applied pulses. In addition, the surface morphology observed after an overall time of 3.2 s at 1.2 V is also comparable to what observed on HOPG after a traditional CV (Fig. S1b). The latter round-sweeps the EC potential from 0.3 V to 1.3 V with typical scan rates of  $10 \div 100 \text{ mV/s}$ , preferably  $25 \text{ mV/s}$ . This means that the CV range close to 1.2 V (region A in Fig. 1 of the main text) is scanned in the order of some seconds (8 s with  $v_{\text{scan}} = 25 \text{ mV/s}$ ). Despite NPV and CV techniques use different approaches, the graphite WE stays at 1.2 V for a comparable time interval in both the experiments. Few differences on surface roughness and blister sizes are beyond the present investigation.



**Figure S1.** EC-STM  $300 \times 300 \text{ nm}^2$  image ( $I_{\text{tunnel}} = 1.0 \text{ nA}$ ;  $V_{\text{bias}} = 0.3 \text{ V}$ ). a) image acquired at an EC potential = 0.3 V after a single long pulse of 3.2 s at 1.2 V. b) image acquired at an EC potential = 0.3 V after a traditional CV (see Fig. 1 of the main text). In both panels, the surface morphology is clearly characterized by blisters.

### b) Graphite behaviour resulting from NPV applied below the oxygen potential.

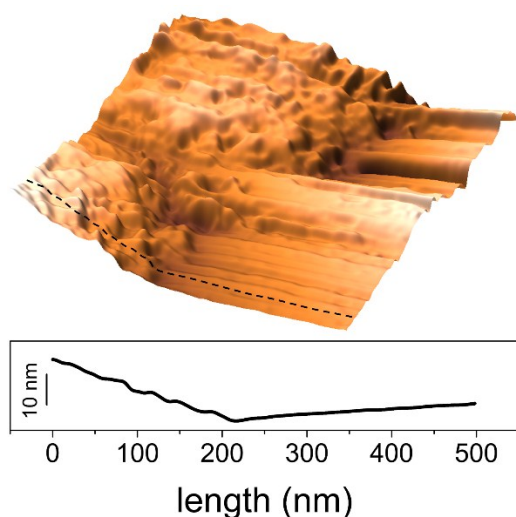
When NPV is applied below the oxygen potential (1.0 V), neither dissolution nor blistering occur. As an example in **Figure S2**, we applied 0.75 V to the graphite WE for a time interval of 1.6 s, which is a long pulse sufficient for both graphite dissolution and surface swelling at higher potentials (i.e. 1.2 V). When the Faradaic current is almost zero, graphite is then stable in the electrolyte.



**Figure S2.** EC-STM 500 x 500 nm<sup>2</sup> image ( $I_{\text{tunnel}} = 1.0$  nA;  $V_{\text{bias}} = 0.3$  V). Image acquired on a HOPG crystal at EC potential = 0.3 V, after a pulse of 1.6 s at 0.75 V. The surface morphology shows flat terraces characteristic of the unperturbed graphite basal plane.

### c) Blister evolution by NPV at 1.0 V.

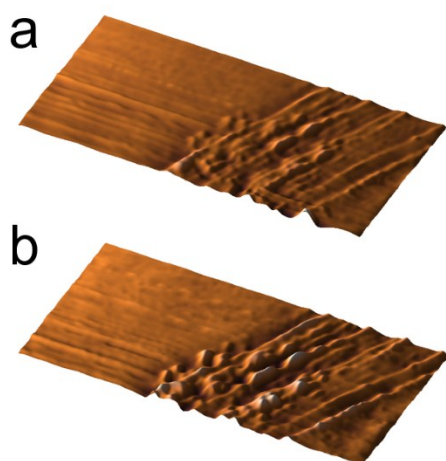
As reported in Figure 5a of the main text, the blister initial growth stage is observed at 0.4 s, when the graphite basal plane is just swelled (see the profile). If the sample undergoes subsequent pulses for a cumulative time interval of, e.g., 1.6 s, the surface morphology is affected significantly by bigger blisters, as reported in **Figure S3**. The latter can be roughly compared with those ones observed after a pulse of 3.2 s at 1.2 V.



**Figure S.3** EC-STM 500 x 500 nm<sup>2</sup> image ( $I_{\text{tunnel}} = 1.0$  nA;  $V_{\text{bias}} = 0.3$  V). Image acquired on an HOPG crystal at EC potential = 0.3 V, after a pulse of 1.6 s at 1.0 V. Graphite is affected by blisters.

### d) Graphite behaviour resulting from NPV applied at the oxygen potential for 0.2 s.

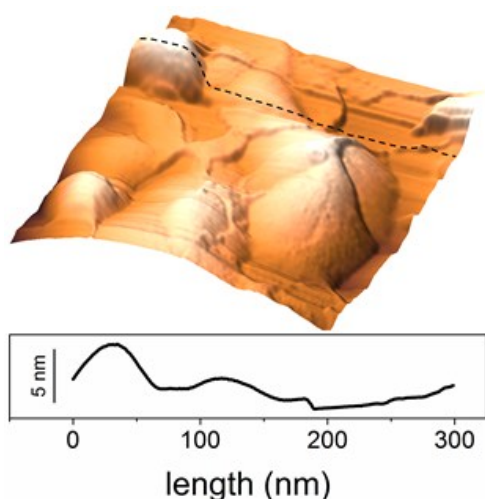
If a 0.2 s-pulse is applied at 1.0 V to the graphite electrode, its surface gets dirty, but the EC-STM does not reveal blisters (compare **Figure S4a** and **b**, the latter acquired about 5 minutes after the former). Here, we do not observe a significant dissolution of the graphite terraces (like the one showed in Fig. 3 of the main text). The qualitative difference between the HOPG morphologies after a 0.2 s-pulse at 1.0 V and after the same time interval at 1.2 V suggests that the amount of carbon atoms dissolved in solution is significantly larger in the latter case. Nonetheless, a carbon quantitative evaluation is difficult to obtain.



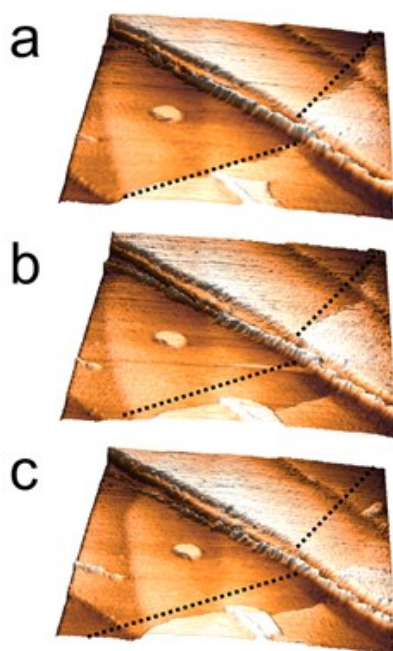
**Figure S4.** EC-STM 400 x 200 nm<sup>2</sup> image ( $I_{\text{tunnel}} = 1.0$  nA;  $V_{\text{bias}} = 0.3$  V). a) Image acquired on an HOPG crystal at EC potential = 0.3 V, after a pulse of 0.2 s at 1.0 V. b) same surface region imaged after 5 minutes. HOPG steps appear dirty, but terrace dissolution is negligible. No graphite swelling or blisters are observed.

#### e) Images of the main text in the 3-D format.

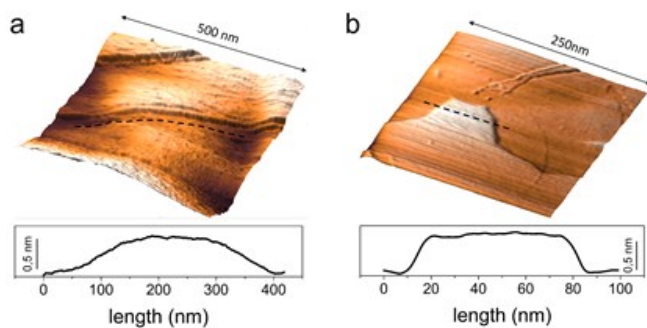
Here, we report the 3-D format of the images shown in the main text in view of enhancing the carbon dissolution, the basal plane swelling and the blister evolution.



**Figure S5.** 3-D format of Figure 2 (see the main text). EC-STM 300 x 300 nm<sup>2</sup> image ( $I_{\text{tunnel}} = 1.0$  nA;  $V_{\text{bias}} = 0.3$  V). Image acquired at an EC potential = 0.3 V after a sequence of 16 pulses (each of them of 200 ms for a cumulative time of 3.2 s) at 1.2 V. The surface morphology is clearly characterized by blisters.



**Figure S6.** 3-D format of Figure 3 (see the main text). EC-STM  $300 \times 300 \text{ nm}^2$  images ( $I_{\text{tunnel}} = 1.0 \text{ nA}$ ;  $V_{\text{bias}} = 0.3 \text{ V}$ ). a) image acquired at an EC potential =  $0.3 \text{ V}$  after a pulse of  $200 \text{ ms}$  at  $1.2 \text{ V}$ . The dotted lines mark the initial position of the edges of two terraces. b) image acquired  $60 \text{ s}$  after (a). c) image acquired  $120 \text{ s}$  after (a). The terrace dissolution is clear from a direct comparison of the surface edges with the dotted lines.



**Figure S7.** 3-D format of Figure 5 (see the main text). a) EC-STM  $500 \times 500 \text{ nm}^2$  images ( $I_{\text{tunnel}} = 1.0 \text{ nA}$ ;  $V_{\text{bias}} = 0.3 \text{ V}$ ). Image acquired at an EC potential =  $0.3 \text{ V}$  after a pulse interval of  $0.4 \text{ s}$  at  $1.0 \text{ V}$ . The surface morphology is characterized by terrace swelling and blisters, as enhanced by the profile acquired along a graphite terrace. b) EC-STM  $250 \times 250 \text{ nm}^2$  images ( $I_{\text{tunnel}} = 1.0 \text{ nA}$ ;  $V_{\text{bias}} = 0.3 \text{ V}$ ). Image acquired at an EC potential =  $0.3 \text{ V}$  after a pulse interval of  $0.4 \text{ s}$  at  $1.2 \text{ V}$ . The surface morphology is characterized by flat terrace, as enhanced by the profile acquired crossing a graphite terrace.