

Electronic Supplementary Material

Stratigraphic analysis of intercalated graphite electrodes in aqueous inorganic acid solutions

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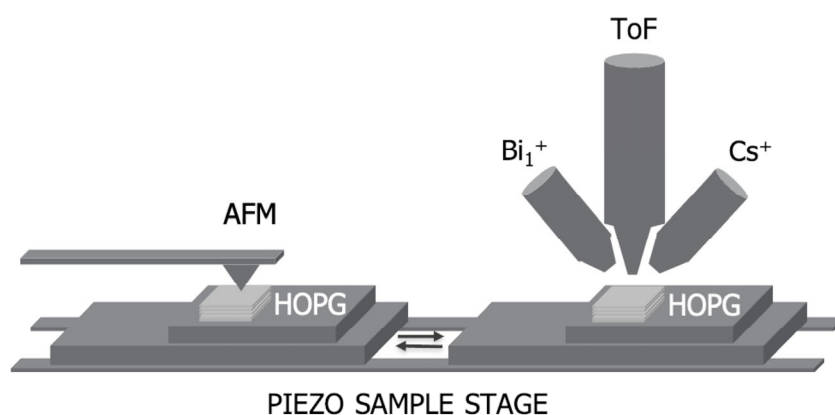


Figure S1 Schematic representation of the correlative ToF-SIMS/AFM system.

In Figure S1, the scheme of the correlative ToF-SIMS/AFM setup is shown. The piezo sample stage has a sub-micron position accuracy that allows a precise positioning from ToF-SIMS to AFM position within the same ultra-high vacuum chamber. A more detailed description of the combined tool was recently reported by Spampinato et al. [1]. In Figure S2, depth profiling experiments for untreated HOPG samples are reported. The elemental and molecular ion signal intensity for C_6^- , O_2^- , Cl^- , S^- , and CO_2H^- is represented as a function of depth. As reported in the literature [2], the C_6^- signal can be used as a reference secondary ion for graphite; it is also depicted in each panel of Figure 3 of the main text for clearness. The O_2^- , Cl^- , S^- , and CO_2H^- compounds, which we expect to measure on the EC treated and immersed samples, show negligible intensities close to the detection limit (blue shaded area). The latter is reported in spectra in the main text for a better evaluation of the data.

Sulfur and chlorine are present on the crystal surface in elemental form (S^- , Cl^-). Their signal intensities decrease in intensity very rapidly together with O_2^- ion signal. Contamination from sulfur and chlorine in both elemental forms and as compounds can occur when the HOPG surface is exposed to the atmosphere [3].

As discussed at the end of the manuscript, circular spots - not showing the graphite symmetry - clearly arise from the intercalated anions. To give a rationale of such kind of features, we add the following image (Figure S3) in the revised Supplementary Materials. Figure S3 reports both the topography and the phase-contrast image (AFM in tapping mode acquisition), which is more sensible to possible surface adsorbates, acquired on the graphite sample when immersed inside the electrolyte.

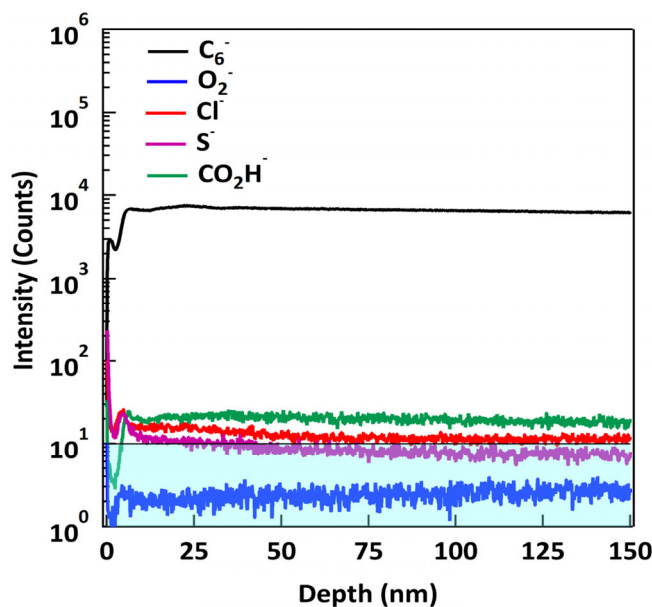


Figure S2 Depth profile of a pristine HOPG sample. Secondary ion intensities of C₆⁻ at m/z 72, O₂⁻ at m/z 31.99, Cl⁻ at m/z 34.96, S⁻ at m/z 31.97, and CO₂H⁻ at m/z 44.99 are plotted versus depth.

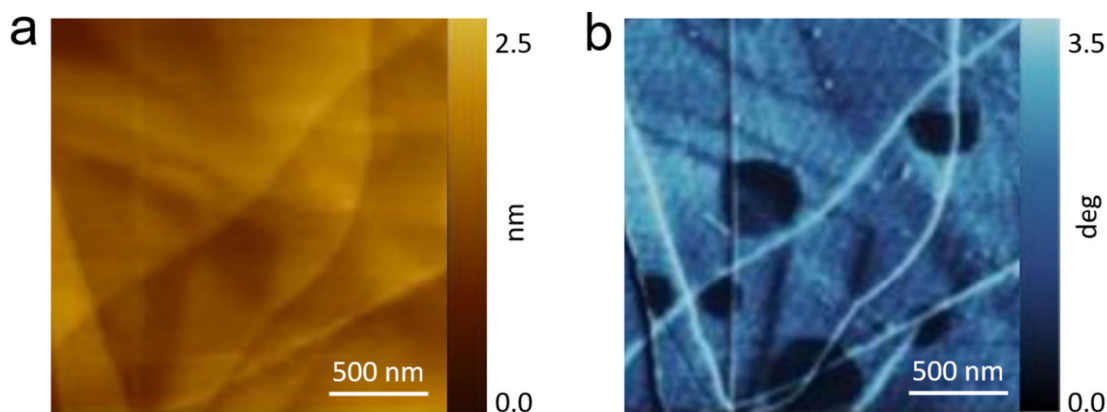


Figure S3 In-situ topography (a) and phase-contrast (b) images of the HOPG electrode immersed in sulfuric acid electrolyte

References

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- [2] Xie, W.; Weng, L.-T.; Ng, K. M.; Chan, C. K.; Chan, C.-M. Defects of clean graphene and sputtered graphite surfaces characterized by time-of-flight secondary ion mass spectrometry and X-ray photoelectron spectroscopy. *Carbon* **2017**, 112, 192-200.
- [3] Martinez-Martin, D.; Longuinhos, R.; Izquierdo, J. G.; Marele, A.; Alexandre, S. S.; Jaafar, M.; Gómez-Rodríguez, J. M.; Bañares, L.; Soler, J. M.; Gomez-Herrero, J. Atmospheric contaminants on graphitic surfaces. *Carbon* **2013**, 61, 33-39.