Supporting Information for the article "Adsorption Behavior of 5-fluorouracil on Au (111): an *in-situ* STM Study"

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In this supplementary information we added extra CV experiments in a high defect-density single crystal and STM images of low defect-density single crystal (large (111) terraces) in phase II under very low tunneling currents.

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CV of a high defect-density Au(111) single crystal

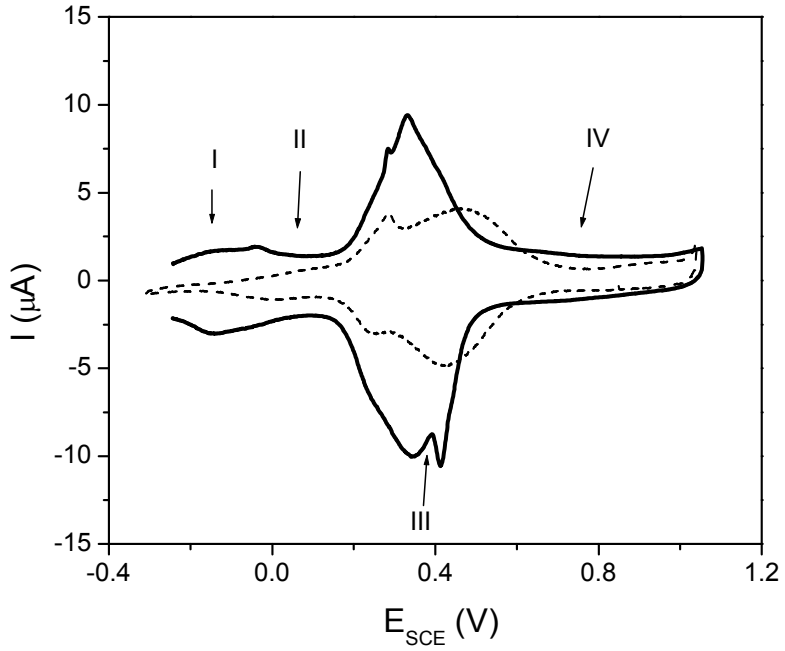

Figure S1. Steady state cyclic voltammogram of the system 6 mM 5FU/50 mM H_2SO_4 /Au(111). Scan rate 50 mVs^{-1}. Continuous lines are with 5FU and dashed without 5FU. This single crystal presents a higher defect density compared to the one present in Figure 1.

Figure S1 presents a steady state CV of a high defect-density single crystal of the systems 6 mM 5FU/50 mM H_2SO_4/Au(111) and 5FU-free (dashed lines). The phase transitions peaks are broaden due to the high defect-density of this single-crystal.[1] The sharp current peak of the transition I↔II could not be detected but just a broad feature circa - 40 mV/SCE. Further potential increase leads to a broad current peak centered at 330 mV/SCE superimposed on a sharp one at ~ 280 mV/SCE, which we assign to phase transitions between phases III-IV and phases II-III, respectively. Even at the highest bulk concentration (up to 36 mM) no spike in the CV could be resolved.

The 5FU-free CV (dashed lines in Figure S1) shows the characteristic features expected for this system. The peak at ~ 280 mV/SCE is due to the reconstruction lifting. The absence of a sharp peak at ~ 800 mV/SCE of disorder/order sulfate adlayer phase transition, which is sensitive to the amount of defect density,[12] corroborates the assignment of a high defect-density single crystal

STM images with low tunneling current

In Figure S2, STM images of the system 18 mM 5FU/50 mM H_2SO_4/Au(111) are presented. All the images are within substrate potentials of the phase II. If there were a 2D flat-flying periodic structure, features with a periodicity approximately 0.7 nm could be imaged characteristic of uracil derivative adlayers on Au(111).[3] However, only the substrate lattice could be imaged, even with the lowest achievable tunneling current (66 pA). In Figure S2a the reconstruction lines of the Au(111) can be clearly seen with regions with high level of noise and regions showing some periodic pattern. Figure S2b is the zoomed in and filtered region of the periodic pattern of Figure S2a. The periodicity is the same of the Au-Au distance (0.27 nm) indicating that we are imaging the substrate (111) lattice. In Figure S2c, the image was taken after sweeping the potential from phase IV to phase II, with the tip relocated and raised for ca. 30 min and then imaging started. Even though in this scheme we had a lower noise level, it was not possible to image the ordered adlayer at any resolution level but only the substrate lattice at atomic resolution.

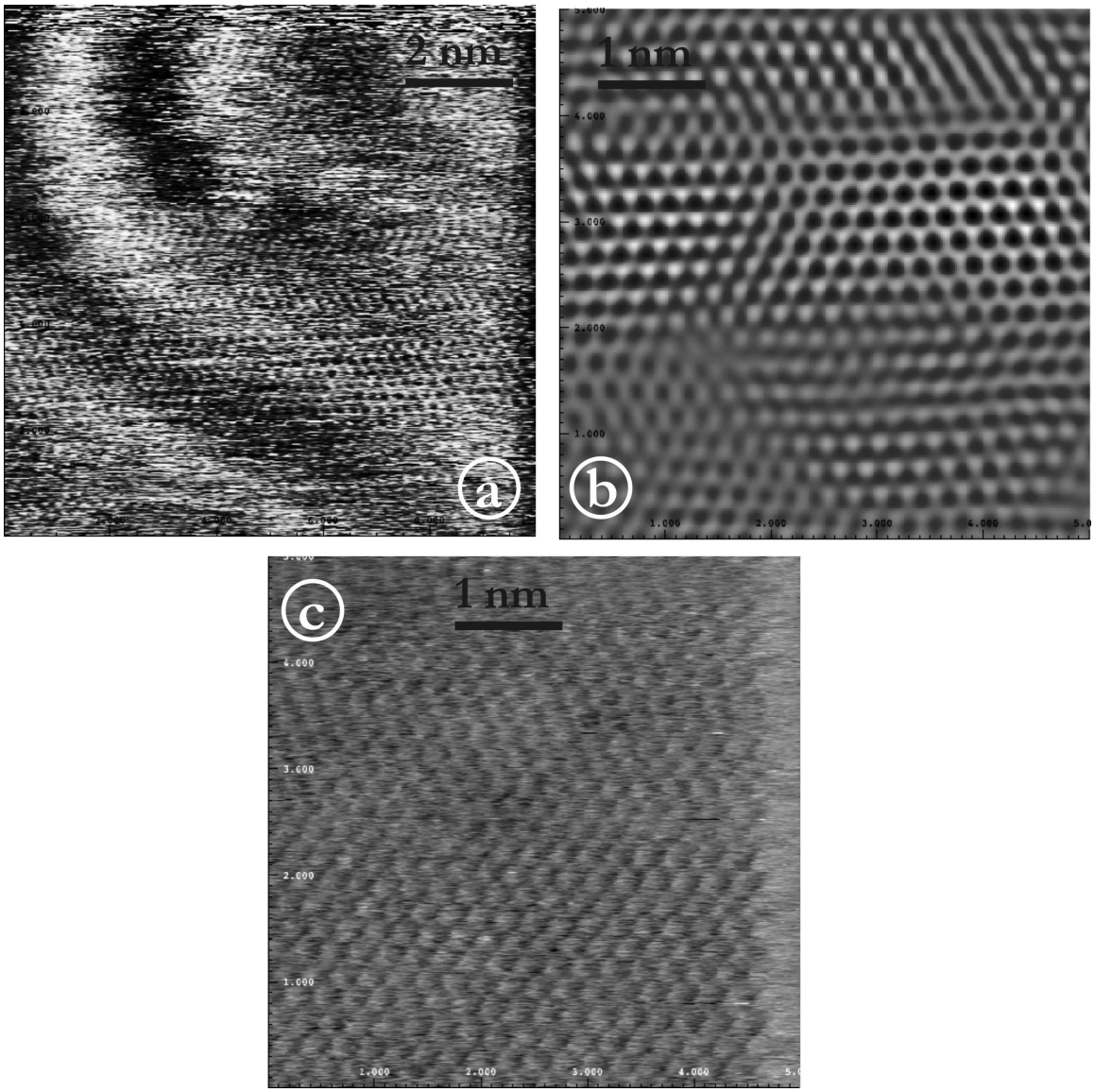

Figure S2. *In-situ* STM images of the system 18 mM 5FU/50 mM H_2SO_4/Au(111). a) E_s = 100 mV, I_t = 66 pA. b) zoomed in and filtered image from a). c) E_s = 150 mV, I_t = 0,72 nA. All potentials are quoted relative to SCE.

References

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