

Self-assembly of methionine on noble metal surfaces: steering biomolecular nanostructures by substrate reactivity and thermal activation

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Molecular self-assembly on surfaces yields promising pathways for the design of functional architectures at the nanoscale [1]. Notably the use of biologically relevant species, such as amino acids or nucleic acids with their inherent qualities as building blocks for the conception of nanostructures, led to fundamental discoveries in the domain of molecular recognition and organization [2, 3, 4]. In general, the state of stable configurations at thermodynamic equilibrium is not only defined by intermolecular interactions, but also by the influence of the underlying support.

Here we report a low-temperature scanning tunneling microscopy (STM) study on the self-assembly of the amino acid methionine under ultra-high vacuum conditions. Methionine provides functionalities which are both relevant for zwitterionic self-assembly and for metal binding sites in peptide chains. We employed two different close-packed metal substrates Ag(111) and Cu(111) with chemical nature. On Ag(111) the molecules dimerize and self-assemble in extended one-dimensional nanostructures running parallel to the closed-packed crystallographic orientations of the underlying atomic lattice (fig. 1) [5]. These commensurate chains arrange mesoscopically into regular biomolecular gratings whose mesoscopic ordering can be tuned by the molecular coverage, as confirmed by STM and complementary helium atomic scattering (HAS) observations. The combined STM and X-ray photoemission spectroscopy (XPS) analysis demonstrates zwitterionic self-assembly over a wide temperature range. By contrast, on Cu(111) the molecular ordering is strongly influenced by the reactivity of the substrate. At low temperatures (243 K) disordered molecular clusters evolve for submonolayer coverages, whereas the saturated monolayer exhibits partial ordering arising from the influence of the substrate, with linear structures growing with a -10° shift with respect to the $\langle 110 \rangle$ crystalline orientations (fig. 2a). On the other hand, following deposition on the substrate held at 303K, a regular one-dimensional phase arises with a $+10^\circ$ shift with respect to the $\langle 110 \rangle$ orientations (fig. 2b) coexisting with patches of the disordered phase. Molecular resolution measurements of the ordered 1D arrangements indicate dimerization and a second-order commensurability with the atomic lattice of the substrate along the chain direction. These results are confirmed by HAS observations. The combined STM/XPS data show that the disordered phase comprises the molecules in their anionic state, with a deprotonated carboxylic group and a neutral amino group, whereas the ordered phase reflects zwitterionic self-assembly.

Finally, the regularity and tunability of the methionine nanogratings on Ag(111) was used for the confinement of the surface state electrons [6], and to steer the positioning of single Fe and Co adatoms in molecular trenches at low temperatures (fig. 3). STM data sequences were obtained to monitor the restricted thermal motions of the confined transition metal atoms that experience a complex lateral energy landscape.

References:

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Figures:

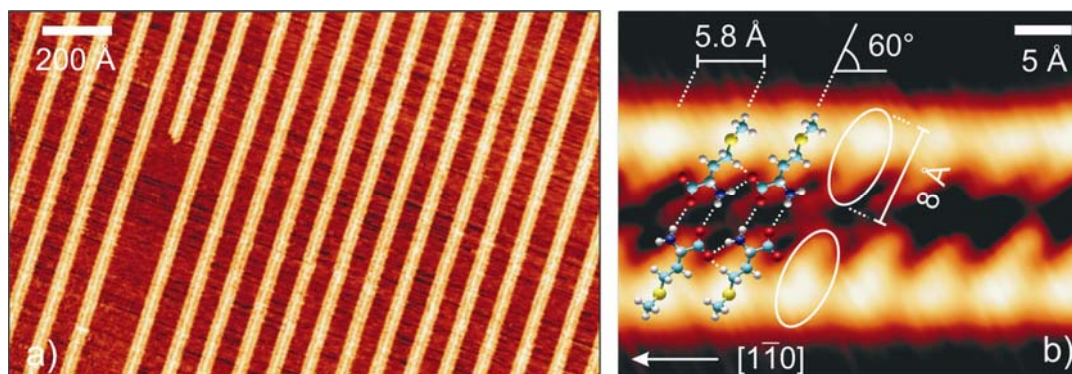


Figure 1 – STM images of the self-assembly of the *L*-methionine amino acid on Ag(111). (a) Regular and tunable 1D biomolecular nanogratings with a periodicity of 94Å ($I = 0.1\text{ nA}$, $U = -500\text{ mV}$, $\theta = 0.38\text{ ML}$). (b) Molecular resolution imaging shows molecular dimerization and commensurate growth along the closed-packed crystalline orientations ($I = 0.9\text{ nA}$, $U = -80\text{ mV}$).

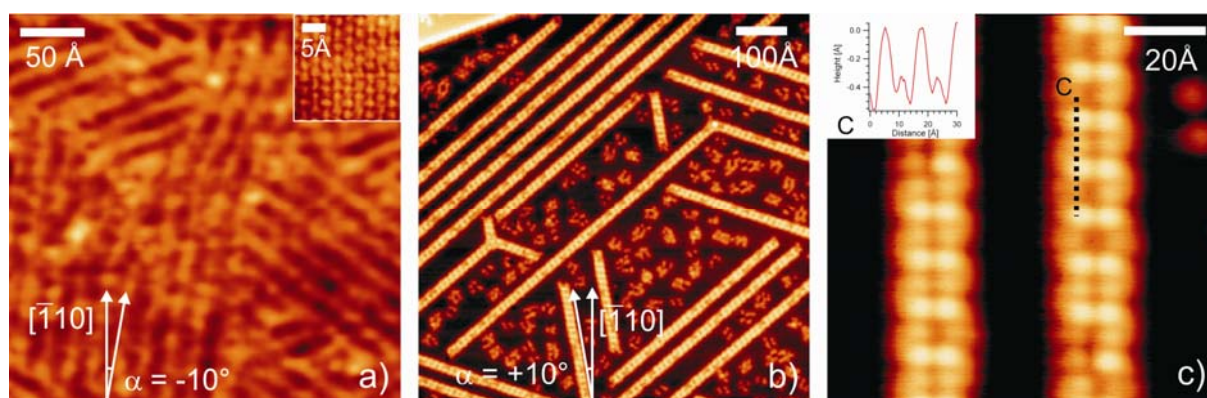


Figure 2 – *L*-Methionine on Cu(111). (a) Saturated monolayer deposited with the substrate held at 243K: molecular structures grow with a -10° with respect to the $\langle 110 \rangle$ crystalline orientations. Inset shows atomic resolution of the Cu(111) substrate ($I = 0.05\text{ nA}$, $U = -100\text{ mV}$). (b) Deposition at 303K shows commensurate 1D ordering with a $+10^\circ$ shift with respect to the $\langle 110 \rangle$ crystalline orientations. The disorder phase is still present ($I = 0.1\text{ nA}$, $U = -500\text{ mV}$). (c) Molecular resolution of the ordered phase shows 2×2 Moiré pattern due to the structure commensurability along the growth direction. Inset: height profile along line C ($I = 0.1\text{ nA}$, $U = -600\text{ mV}$).

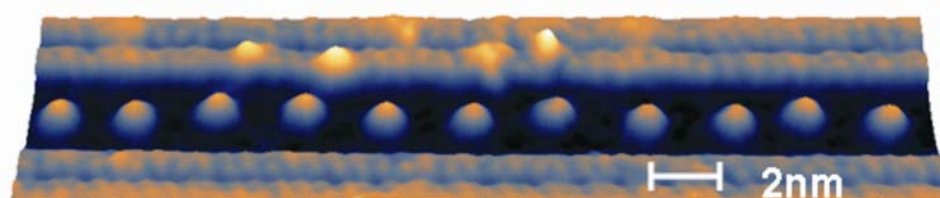


Figure 3: Self-alignment of Fe adatoms between *L*-methionine rows on Ag(111) at 18K.