

THE STRUCTURE OF ALKANETHIOLS MONOLAYERS SELF-ASSEMBLED ON GOLD

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We have determined the structural configuration of Alkanethiols $[(\text{CH}_2)_n\text{CH}_3\text{SH}]$ on gold, a puzzling issue that was raised almost 15 years ago in Princeton and that we have finally solved in Trieste by a concerted experimental and theoretical effort. Alkanethiols on gold represent the archetypal among self-assembled monolayers (SAMs), since they form a strong link to the metal substrate through the thiol head-group, while the tail-group can be easily functionalized to tailor the SAM properties, such as wetting, corrosion, adhesion, lubrication and conductivity. At the same time, gold, being unreactive and biocompatible, can be easily patterned, and obtained as a colloid, as nanoclusters and as a thin film. In the latter case, the surface of the individual grains prevalently displays the high symmetry (111) crystal face.

Common to all alkanethiols on Au(111) is the formation of an ordered SAM displaying a hexagonal $(\sqrt{3}\times\sqrt{3})$ symmetry, corresponding to the adsorption of one standing-up molecule each three Au atoms. Long-chain alkanethiols display an additional modulation of the $(\sqrt{3}\times\sqrt{3})$ structure, yielding a $c(4\times 2)$ superlattice with the same molecular concentration. These densely packed ordered phases can be equivalently obtained by adsorption from the vapor-phase or in dilute solution, which explains the widespread employment of this system in many research fields. [1]

Even if alkanethiols on Au(111) are by far the most studied SAMs, the exact determination of the adsorption site of sulphur gave rise to a longstanding controversy. First, ab initio calculations were supporting the adsorption of

thiols with S in between two Au atoms (bridge site), whereas experiments of photoelectron and photon interference between S and Au atoms rather indicated the presence of sulphur on-top of single Au atoms. Second, the formation of the $c(4\times 2)$ superlattice implies that the SAM must be formed by molecules adopting two different orientations or adsorption sites.

Recently we have studied the SAM structure of methylthiol (CH_3SH), MT, the simplest and yet the most disputed one. By a recursive comparison between diffraction measurements (x-rays and photoelectrons) and molecular dynamics calculations, we have found a model consistent with ours and former experiments, where the simple $(\sqrt{3}\times\sqrt{3})$ structure results from the dynamical equilibrium between thiols adsorbed in two different, but interchangeable configurations. One configuration is formed by a thiol in a bridge site, the other is formed by two thiols that pull an Au atom out of the surface yielding a staple structure, where the S atoms are laterally linked to the common Au adatom, but they sit almost on-top of a surface Au atom. This novel structure is made energetically competitive with the bridge site by the presence of vacancies. [2]

Due to the fast Au surface diffusion, the Au vacancies produced by the staples are rapidly delocalized over the surface. The vacancy diffusion favors the interchange between bridge and staple configurations (on a picosecond timescale at room temperature). The dynamical disorder due to diffusing vacancies and thiol interchange prevents the establishment of a long range correlation between the bridge and staple thiols, yielding an average $(\sqrt{3}\times\sqrt{3})$

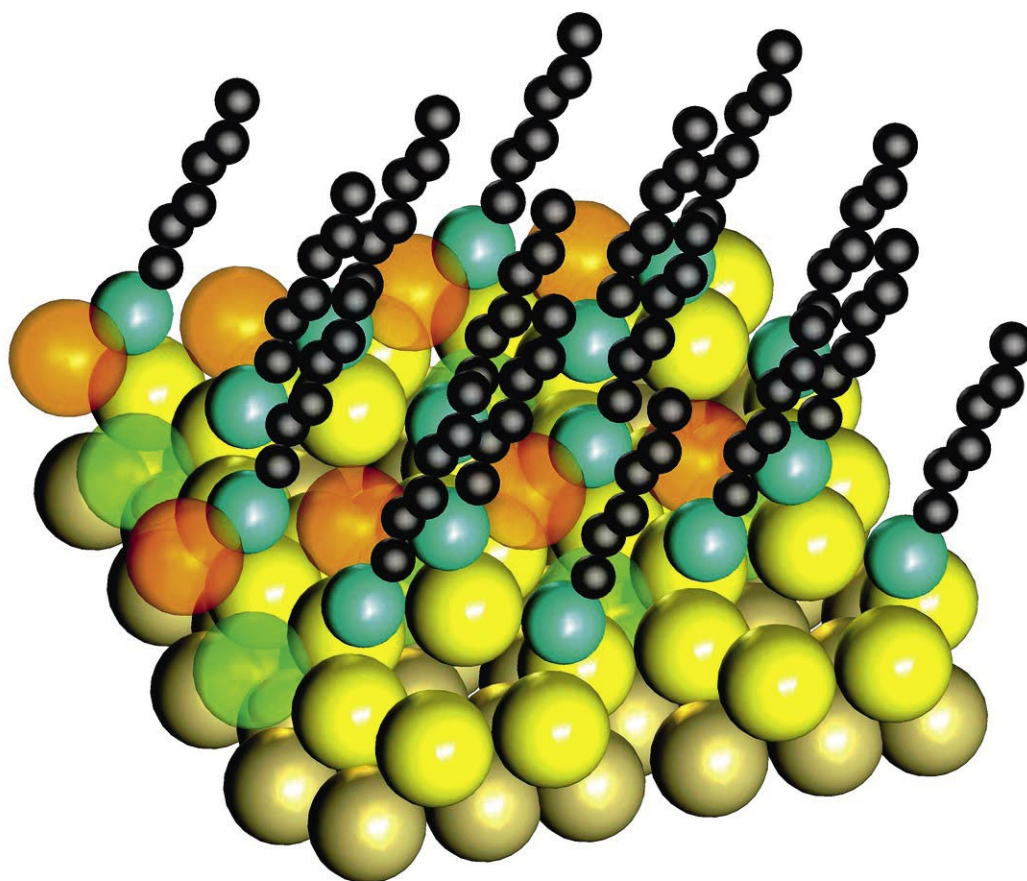


Figure 1. 3D pictorial of the $c(4 \times 2)$ structural model resulting from x-ray diffraction fit. Hexanethiols (S in light-blue, C in black) in bridge and staple configurations are shown; surface Au atoms in yellow, Au adatoms in orange. Partially occupied Au positions are indicated by transparent atoms (surface atoms in green, adatoms in orange).

symmetry, that simply leads to an MT coverage of one molecule every three surface Au atoms. [2]

Once verified for the case of methylthiol, we tested the predictive strength of our model on long-chain alkanethiol SAMs, which display the more complex $c(4 \times 2)$ superlattice. We have considered the case of hexanethiol $[(\text{CH}_2)_5\text{CH}_3\text{SH}]$, HT, which intermediate length yields a SAM with coexisting $(\sqrt{3} \times \sqrt{3})$ and $c(4 \times 2)$ phases. Both molecular dynamics calculations and x-ray diffraction measurements indicate that the HT SAM contains the same ingredients of the MT one, i.e. Au vacancies, Au adatoms, and thiols, in both bridge and staple configuration. In this case, however, the dynamical disorder at the surface is strongly hampered by the van der Waals' interaction among the tails of the HT molecules. Calculations predict an effective slowing of the interchange mechanism. With respect to MT, the longer living staple and bridge HT configurations allow the establishment of a correlation among them and the vacancies, that gives rise to the $c(4 \times 2)$ symmetry phase. Experimentally, the atomic disorder of the surface layer is partially quenched yielding a vacancy delocalization much lower than in the

MT case. The adatoms in the staple configuration are found to line-up yielding the characteristic zig-zag arrangement of the molecules (Figure 1). [3]

In conclusion, thiols on the Au(111) surface are found to adsorb in two different geometric configurations and to produce a dynamical disorder by creating adatoms and vacancies that rapidly diffuse over the surface. The van der Waals' interaction among the tails of long chain alkanethiols drives the ordering of the thiols, hence reducing the dynamical disorder on the Au surface.

References

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