Modeling Self-Assembly of Phosphonic Acids on α-Aluminum Oxide

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Computational modeling of diffusion-limited processes such as the formation of self-assembled monolayers (SAMs) is still a challenging task due to the large timescales. [1] Here, we present a modified Kawska-Zahn approach, [2] in which steered dynamics simulations and Monte-Carlo steps are combined to mimic chemisorption of various phosphonic acids (PAs) on the α-Al_2O_3 (0001) surface.

Our studies reveal that in vacuum the aliphatic PA molecules first form patches on the surface, analogous to the striped phase in the early stage of SAM formation of alkanethiols on gold. [3] Subsequent adsorption leads to a disordered amorphous phase with a high concentration of gauche defects from which ordered domains emerge upon further adsorption. In 2-propanol, by contrast, the unpolar chains do not cling to the polar surface as they are better stabilized by the solvent. Thus the overall order of the wet SAM is higher than in the dry state.

In agreement with experimental evidence from Peukert *et al.*, the simulations show that molecules from solution are also incorporated in inverted adsorption geometry with the PA anchor remaining solvated. These loosely bound molecules increase order when the solvent is evaporated, but are dissolved again after subsequent re-immersion, whereby the ordering in the monolayer is diminished. Repeated de-wetting and re-immersion can hence improve the SAM quality as molecules bound in inverted adsorption geometry are dissolved and reincorporated into the monolayer in correct binding geometry. [6]

[1] M. L. Klein, W. Shinoda, *Science*, **2008**, *321* (5890), 798-800.
[2] A. Kawska, J. Brickmann, R. Kniep, O. Hochrein, D. Zahn, *J. Chem. Phys.*, **2006**, 124, 24513.
[3] G. E. Poirier, E. D. Pylant, *Science*, 1996, *272* (5265), 1145-1148.
[4] C. M. Jäger, T. Schmaltz, M. Novak, A. Khassanov, A. Vorobiev, M. Hennemann, A. Krause, H. Dietrich, D. Zahn, A. Hirsch, M. Halik, T. Clark, *J. Am. Chem. Soc.*, **2013**, *135* (12), 4893-4900.
[5] C. Meltzer, J. Paul, H. Dietrich, C. M. Jäger, T. Clark, D. Zahn, B. Braunschweig,W. Peukert, *J. Am. Chem. Soc.*, **2014**, *136* (30), 10718-10727.
[6] C. Meltzer, H. Dietrich, D. Zahn, W. Peukert, B. Braunschweig, *manuscript submitted for publication*, **2015**.