Formation of enantioselective molecular structures on the PdGa:A(-1-1-1)Pd_3 surface

Stolz Samuel, Widmer Roland

EMPA, nanotech@surface, Überlandstrasse 191, 8600 Dübendorf, Switzerland
samuel.stolz@empa.ch.

Abstract

Intermetallic PdGa has recently attracted considerable interest because of its high activity, selectivity, and stability in the catalytic semi-hydrogenation of ethyne [1], being an important step in the polyethylene production. Owing to its non-centrosymmetric bulk structure of the space group $P2_13$, PdGa exists in two enantiomeric forms A and B [2]. Investigating PdGa{111} surfaces, the stacking sequence in the [111] direction involves four nonequivalent atomic planes. As a consequence, the top and bottom surfaces are different: PdGa:A(111) is terminated by an atomic layer containing one isolated Pd atom per surface unit cell and accordingly this termination is denoted as Pd_1, on the other side, PdGa:A(-1-1-1) reveals isolated Pd trimers and is thus denoted as Pd_3 [3].

To probe the chirality of the Pd_1 and Pd_3 surfaces, 9-Ethynylphenanthrene (9-EP) which is a prochiral molecule is adsorbed on both surfaces. For the Pd_1 surface a highly enantioselective adsorption with an enantiomeric excess of 98% is reported upon 9-EP evaporation at room temperature (RT) [4]. Adsorbing 9-EP at RT on Pd_3 yields in a 1:1 ratio of left and right oriented molecules, thus no enantiomeric excess is observed. However, post-annealing to 500 K of the 9-EP on Pd_3 results in the formation of new structures consisting of three 9-EP molecules in a propeller-like shape. 99.8% of the 9-EP molecules forming the propellers are of the same enantiomeric form, thus 99.3% of all propellers are homochiral with an enantiomeric excess of 98.6%.
Further analysis of these propellers by STM reveal a voltage dependent protrusion in the center of the propeller, which might be explained by a sp2 hybridisation of the C=C-H bonds or by an electronic effect. Therefore, nc-AFM investigations with a CO functionalized tip were performed and will be compared to STM (see Fig. 1) and discussed.

References

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Figure 1: Comparison of 9-EP propellers on Pd3 between STM and nc-AFM