

Molecular self-assembly of covalent nanostructures: Unraveling their formation mechanisms

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Several experimental studies have illustrated how large macromolecular structures can be formed through molecular self-assembly on surfaces. This success has mainly been obtained via trial and error coupled to insights from organic chemistry, and to date there is little theoretical understanding of how covalent self-assembly proceeds on a submolecular level. We work towards this understanding for two important reaction mechanisms.

A successful approach to generate covalently linked nanostructures through self-assembly is to use molecular building blocks with specific hydrogen atoms replaced by bromine atoms [1]. By splitting-off the bromine atoms one enables the molecules to covalently couple into various structures. In a recent experimental study it was illustrated how graphene nanoribbons (GNRs) self-assemble on the Au(111) surface [2]. In a first step, the debromination strategy is employed to create poly-anthracene from a bianthracene derivative. Secondly, poly-anthracene undergoes a cyclodehydrogenation, resulting in the GNR.

Here we aim to obtain a detailed atomistic view into both of these reaction mechanisms from first principles density functional calculations. In a first part, the mechanism of the debromination will be discussed from a more general viewpoint. The reaction has been studied for bromobenzene on the close-packed (111)-facets of commonly used coinage metals, and we illustrate how the different surfaces catalyzes the reaction.

Secondly, the mechanisms controlling the cyclodehydrogenation of polyanthracene into the GNR on Au(111) will be elucidated. The catalytic role of the Au surface will be discussed by comparing possible reaction pathways. We find that the most favorable transition path is associated with only one barrier, while the other conceivable paths have a second high energetic barrier. Finally, we discuss the cooperative effects involved in the subsequent cyclodehydrogenation, showing how the reaction propagates with a domino-like effect throughout the poly-anthracene [3].

[1] L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters and S. Hecht, *Nature Nanotechnol.* 2 (2007) 687.

[2] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen and R. Fasel, *Nature* 466 (2010) 470.

[3] J. Björk, S. Stafström and F. Hanke, *J. Am. Chem. Soc.* 133 (2011) 14884.