On-surface switching off and on of Ullmann coupling by molecular gases

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Ullmann coupling reaction has been attracted great interest in the last decades due to the advantage to build 1D-2D nanostructures from bottom-up fabrication like graphene nanoribbons, polymer, etc…[1]. This reaction, it is used to generated covalent molecular linked coupling, C-C, by different halogen molecule precursors. The reaction is activated by the substrate, where the precursors will be dehalogenated. Thus, the substrate plays an important role in the success of the reactions. There are several challenges, one of them is the scaling-up production of high quality nanostructures, where defects or co-adsorbates can reduced the success of this process. It has been reported two cases, where the Ullmann coupling reaction are partially inhibited [2, 3]. Here, we reported for the first time the reactivation of the reaction after inhibited on Au(111) by molecular gases.

In this work we describe a variable temperature Scanning tunnelling microscopy (VT-STM) study that allows us to identify the switch on and off of the Ullman coupling reaction of this molecule (2,8-Dibromodibenzothiophene) on Au(111). After low temperature deposition on pristine Au(111), the results show that surprisingly Ullmann coupling mechanism happen even at 100 K. We speculate that the modification of the herringbone reconstruction due to the strong interaction between S and Au atoms, can facilitate the lifting of the Au adatoms inducing the reaction even at low temperature. On the other hand, when we firstly dose sulfur atoms on the pristine gold crystal by H_2S vapor and subsequently depositing DBDBT molecules, the Ullmann coupling reaction has been completely inhibited due to the formation of S-Au complexes, which is blocking the activation of the reaction due to the gold adatoms on the terrace and step-edges are not available. Dysprosium and Iodine atoms have reported similar partial inhibition on silver and copper, respectively. However, we are able to reactivate the reaction by removing the sulfur atoms from the substrate by exposing the sample to H_2 (gas). STM images show again the Ullmann coupling reaction has been switched on. This result shows the important of co-adsorbates on the substrate and also emphasizes the strong interaction between substrate adatoms (terraces and step edges) and the molecule precursors during the dehalogenation reaction.

References:
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