Bottom-up formation of molecular wires on a semiconducting oxide:
Aryl halides covalent coupling controlled by surface hydroxyl groups on rutile TiO_2 surfaces

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Abstract

Molecular nano-architectures formed by the on-surface chemical reactions have attracted great attention over the last few years [1-3]. The bottom-up strategies allow assembling of covalently coupled molecular structures of well-defined morphologies, including: molecular wires, 2D molecular networks, or confined graphene nanostructures. So far, surfaces of selected noble metals have been mostly used as substrates. Recently we could demonstrate for the first time the feasibility of the on-surface covalent coupling of aryl halide precursors on a semiconducting oxide. Low temperature STM (LT-STM) studies and DFT-D modelling showed that thermally activated 10,10'-dibromo-9,9'-bianthryl (**DBBA**) monomers form polyanthrylene chains on the rutile TiO_2(011)-(2x1) surface [4].

Following our recent work, here, we report on the role of surface hydroxyl groups in the on-surface polymerization on rutile TiO_2(011) and demonstrate univocally that OH groups are in this case essential for the reaction to occur [5]. We show that the polymerization of diiodoterfluorene (**DITF**) molecules proceeds most effectively when the reduced TiO_2(011) is prepared with a moderate density of surface hydroxyls(~5% coverage), leading to formation of long molecular wires. Increasing the density of the surface hydroxyls (to ~20%) by surface exposure to atomic hydrogen results in formation of shorter oligomers, whereas the hydroxyl-free surface (<0.5%) suppresses the polymerization reaction completely. These results are in agreement with the recently proposed C-C coupling mechanism, which involves proton transfer from a surface hydroxyl group to the precursor molecule [4,5].

References

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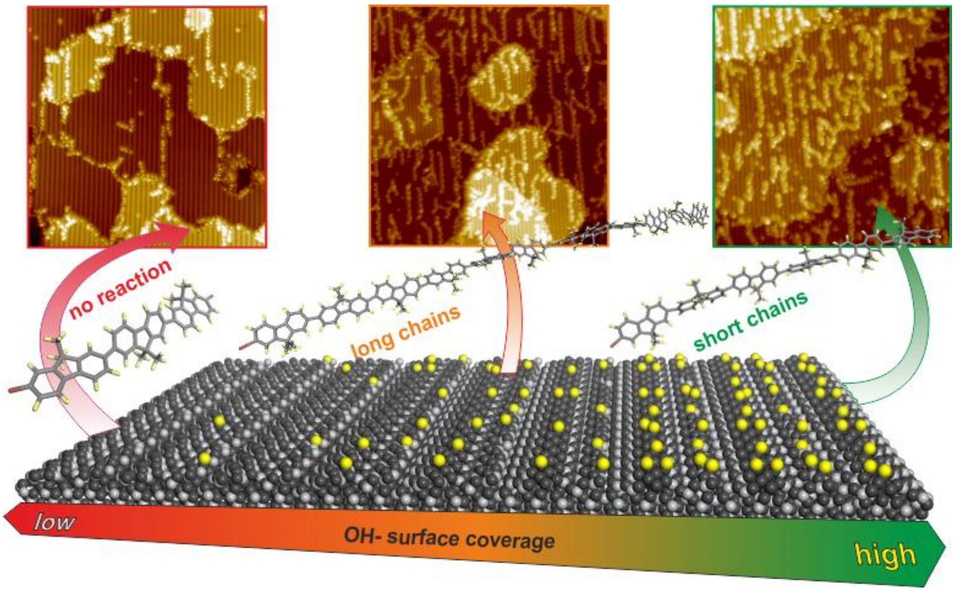

Figure 1. Polymerizing the **DITF** monomers on rutile TiO_2(011) surfaces with varying hydroxyl groups coverage [5].