

On-surface polymerization as a facile method for bottom-up nanoconstruction on inorganic semiconductor substrates

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Over the past years on-surface polymerization, enabling direct connection of a variety of suitable monomer building blocks directly on a given substrate, has emerged as a vibrant field of research. A potpourri of linking reactions giving rise to a large structural and compositional diversity of the prepared 1D and 2D polymer has been explored thus far yet on a limited number of substrates, primarily coinage metal surfaces. This is primarily due to STM analysis used in most investigations as it is greatly facilitated on these noble metal surfaces. Only recently on-surface linking reactions have been carried out successfully on inorganic insulator and, perhaps more appealing, on inorganic semiconductor substrates. Here, we highlight our most recent findings of polymerizing organic monomers via aryl-aryl coupling step-growth in-situ on a particular rutile (TiO₂) surface. We show monomer synthesis, provide evidence for successful on-surface polymerization, and explore crucial reaction parameters. Our findings significantly enhance the scope of our on-surface polymerization method and illustrate its tremendous potential for the bottom-up generation of organic-inorganic hybrid nanostructures.

The bottom-up generation of covalent nanostructures directly on substrate surfaces via the so called “on-surface polymerization” approach, pioneered by us [1], has recently become a very active field in nanoscience. A large variety of well-defined nanostructures including molecular wires [2-4], 2D molecular networks [5-7], or confined graphene nanostructures [8-10] has been generated from suitable

monomers. These precursor molecules possess specific linking sites, which are activated after their deposition on a substrate surface, typically coinage metals (Cu, Ag, and Au). While the noble metal surface facilitates analysis via STM imaging, it also catalyzes activation of the aryl halide monomers as well as coupling of the formed aryl intermediates. However, in particular in the case of preparing π -conjugated polymers on top of the metallic surface their optoelectronic functions are largely sacrificed and hence from the standpoint of practical applications of on-surface covalent coupling, highly ordered semiconducting [11] or insulating [3, 10, 12] surfaces clearly represent much more attractive platforms. In particular inorganic semiconductor surfaces, such as transition metal oxides, present a complementary match for the organic semiconductors formed via on-surface polymerization and offer advantageous optical as well as photo- and electrochemical properties. These properties could potentially be enhanced by an on-surface polymerized organic semiconductor layer and hence resulting in possible applications in photonics, photocatalysis or gas and bio sensing [13, 15]. In this context, titanium dioxide constitutes a privileged inorganic semiconductor, which has attracted lots of attention in the context of dye-sensitized solar cells and photocatalytic water splitting and waste-water detoxification. From a surface science perspective in particular the surface of rutile TiO₂ (011) has been intensely investigated recently [16,17].

For the first time we could recently demonstrate the feasibility of the on-surface covalent coupling of aryl halide

precursors on the rutile $\text{TiO}_2(011)-(2 \times 1)$ surface (Figure 1) [11]. By depositing 10,10-dibromo-9,9'-bianthryl (DBBA) monomers on a $\text{TiO}_2(011)-(2 \times 1)$ surface kept at 270 °C growth of oligomers reaching up to 10 nm chain length and corresponding to ca. 20-mers was observed. In contrast to the process consisting of polymerization followed by intramolecular annulation on Au(111) [8], the latter cyclodehydrogenation reaction could not be induced on the $\text{TiO}_2(011)-(2 \times 1)$ surface leading to formation of polyanthrylene and not narrow armchair-type graphene nanoribbons. However, the successful covalent coupling of aryl halides on the $\text{TiO}_2(011)-(2 \times 1)$ surface was encouraging and motivated us to investigate critical parameters in the polymerization process on such non-metallic substrate. In particular, the specifics of the surface, such as reconstruction, redox state of the titanium atoms, and presence of hydroxyl groups was in the focus of our investigations as they represent a major difference to the coinage metals and should strongly affect the operating polymerization mechanism. Furthermore, the monomer was changed to potentially lower the temperature necessary to induce polymerization.

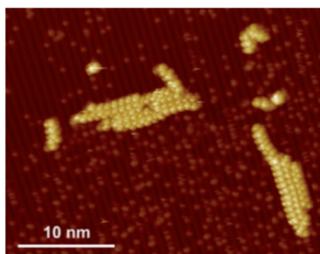
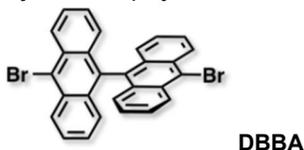


Fig. 1 > Initial polymerization of 10,10'-dibromo-9,9'-bianthryl (DBBA) monomers on $\text{TiO}_2(011)$ [11]./

On the one hand an oligofluorene monomer building block as a well-studied repeating unit in on-surface polymerization [2-4] was equipped with terminal iodine substituents as they were expected to further lower the necessary activation temperature [5]. For this purpose, diiodoterfluorene (DITF) was prepared (Figure 2). Synthesis involves preparation of 9,9-dimethylated terminal fluorenes, which as boronic esters are being coupled to a 2,7-dibromo-9,9-dimethylfluorene core yielding the barely soluble permethylated terfluorene (TF), which is iodinated in the final step of the synthesis.

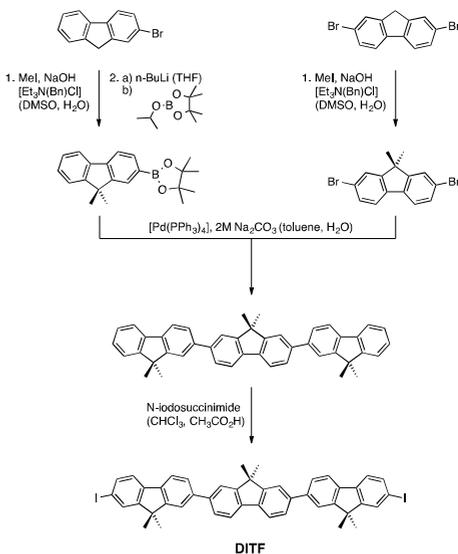


Fig. 2 > Synthesis of diiodoterfluorene (DITF) monomers./

On the other hand, reduced $r\text{-TiO}_2(011)-(2 \times 1)$ surfaces containing various amounts of surface hydroxyl groups were prepared. The (2×1) reconstruction of $\text{TiO}_2(011)$ consists of two-fold coordinated terminal oxygen and five-fold coordinated terminal titanium atoms forming a characteristic zigzag pattern on the rows running along the [01-1]

direction [18]. Hydrogen atom adsorption on the terminal exposed oxygen atoms leads to formation of surface hydroxyl groups [19]. In scanning tunneling microscopy (STM) images these surface hydroxyl groups are observed as bright protrusions located nonsymmetrically on top of the zigzag pattern. Mechanistically, the presence of surface hydroxyl groups should have a dramatic effect on the coupling mechanism as it is assumed to proceed via a surface stabilized aryl radical on coinage metal surfaces. Therefore, one would at first expect hydroxyl groups to possibly terminate polymerization by hydrogen atom abstraction from the outcome of the on-surface polymerization a $r\text{-TiO}_2(011)\text{-}(2\times 1)$ surface containing less than 0.5% coverage of hydroxyl groups was prepared [17]. Note that the coverage is given relative to the maximum number of available two-fold coordinated terminal oxygen atoms. For comparison, two other types of well-defined $r\text{-TiO}_2(011)\text{-}(2\times 1)$ surfaces with medium ($5 \pm 1\%$) and high ($20 \pm 1\%$) hydroxyl group coverage were prepared using atomic hydrogen to react with the $r\text{-TiO}_2(011)\text{-}(2\times 1)$ surface.

Polymerization of the DITF monomers was carried out by evaporation on the differently prepared substrates kept at 260°C . STM analysis of the product mixture on the $r\text{-TiO}_2(011)$ surface as well as an oxidized $o\text{-TiO}_2(011)$ surface revealed that no polymerization took place. This is rather surprising as both surfaces practically do not contain surface hydroxyl groups and hence formed aryl radicals (if formed) should have the opportunity to dimerize, i.e. connect, without termination. On the contrary, upon evaporation of DITF monomers on the two medium and highly hydroxylated $r\text{-TiO}_2(011)$ surfaces leads to formation of polymers (Figure 3),

which adsorb along the surface reconstruction rows. High-resolution STM imaging clearly revealed the bright protrusions of the methyl groups for each fluorene unit and analysis of the observed distances proved covalent connection into polyfluorene chains as previously observed only on coinage metal surfaces [2-4].

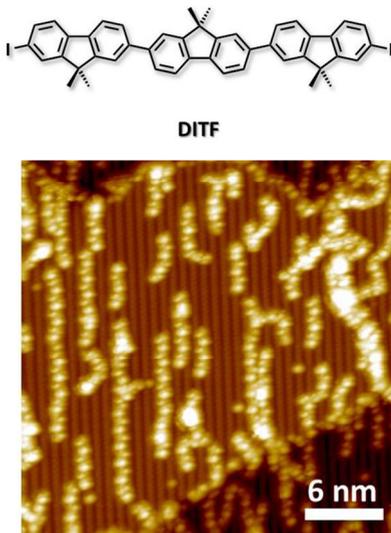


Fig. 3 > Polymerization of diiodoterfluorene (DITF) monomers on a reduced $r\text{-TiO}_2(011)\text{-}(2\times 1)$ surface with medium ($5 \pm 1\%$) hydroxyl group coverage at 260°C .

Interestingly, when comparing STM images before and after polymerization it appears that the surface hydroxyl groups are consumed during the polymerization process. The disappearance of the surface hydroxyl groups must be due linked to the operating polymerization mechanism (or a chemical reaction connected to it) because treating the rutile $\text{TiO}_2(011)\text{-}(2\times 1)$ at these temperatures typically does not lead to desorption of the surface-bound hydrogen atoms [19]. One possible explanation might be trapping of the formed iodine substituents as gaseous H-I. Importantly, polymerizations carried

out on the medium hydroxylated surface yield longer polymer chains as compared to the ones carried out on the highly hydroxylated substrate as revealed from STM image analysis and detailed statistics. Therefore, it seems that there is an optimum coverage of surface hydroxyl groups. It should be emphasized here that defects such terrace edges or domain boundaries act as anchoring sites for the formed oligomers and hence reducing their number should lead to further increase of the polymerization efficiency.

In conclusion, we have experimentally demonstrated the feasibility and generality of on-surface polymerization on partially hydroxylated $r\text{-TiO}_2(011)$ surfaces and investigated critical growth parameters. Based on our experimental findings, a detailed mechanistic rationale is currently being developed. From a more applied perspective our approach should now be applied to grow a large variety of oligomers and polymers on various transition metal oxides and other inorganic semiconductors thereby leading to interesting hybrid systems with matched valence and conduction bands of both organic and inorganic semiconductors.

Acknowledgements

Generous support by European Project "AtMol" is gratefully acknowledged.

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