

Chemically functionalized metal oxide surface: self-assembly of terephthalic acid on rutile $\text{TiO}_2(110)$

J. S. Prauzner-Bechcicki¹ S. Godlewski¹ A. Tekiel^{1,2} F. Zasada³ W. Piskorz³
J. Budzioch¹ P. Cyganik¹ Z. Sojka³ M. Szymonski¹

¹Centre for Nanometer-Scale Science and Advanced Materials, NANOSAM, Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland

²Department of Physics, McGill University, 3600 University Street, Montreal QC, H3A 2T8, Canada

³Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

Many applications of nanotechnology require proper chemical functionalization of surfaces. Stable, flexible and high-quality functionalized surfaces are efficiently manufactured via molecular self-assembly. Such self-assembled monolayers may be used as a direct linker between the monocrystal template and the on-top built structures, for example for on-surface growth of metal organic frameworks (SURMOF). In the presentation, we discuss a self-organization of 1,4-benzenedicarboxylic acid molecules (terephthalic acid, TPA) on a rutile $\text{TiO}_2(110)-(1 \times 1)$ surface, basing on combined experimental and theoretical studies[1-3]. The system in question is analyzed by means of ultra-high vacuum scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM) and periodic density functional theory (DFT) calculations. On the basis of scanning probe microscopy results the model of TPA adsorption on the rutile $\text{TiO}_2(110)-(1 \times 1)$ is proposed and further corroborated with theoretical modeling. It is concluded that TPA molecules are adsorbed in an upright position forming a well-ordered monolayer. Molecules bind to the surface via carboxylic groups as terephthalic anions in a bi-dentate fashion with the two 5-fold coordinated Ti atoms. The second carboxyl group is exposed to the vacuum interface and allows for dimer formation between the adjacent TPA molecules. To elucidate the reactivity of the functionalized surface, we deposit zinc formate ions on top of the compact TPA monolayer in our simulations. Calculations show that the anchoring properties of the TPA/ TiO_2 system are not perturbed by the dimer formation, auguring well for its prospective application as a promising chemically functionalized surface for on-top growth of metal organic frameworks. Furthermore, STM measurements supported by theoretical modeling show that due to specific tip apex modifications it is possible to image different parts of the electronic structure of the dimer TPA/ TiO_2 layer. In particular, it is possible to obtain enhanced contrast of functional groups on top of the molecular layer. The quality and stability of the monolayer are tested,

including the resistance against air exposure. Finally, for the sake of completeness structural properties of TPA deposited at low coverage are discussed[3; 4].

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