Structure, properties, and functionalization of surfaces from the perspective of DFT calculations

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This seminar addresses the topic of the physical and chemical characterization of complex surfaces and interfaces by means of DFT-based simulations, showing how the interplay between theory and experiment can shed light on their properties. In the first part of the seminar, recent progresses on the modelling of two-dimensional dichalcogenides and oxide thin films will be shown. In the second part, the main findings on the functionalization of metal- and metal oxide surfaces with N-heterocyclic molecules will be illustrated.

Mixed-dimensional van der Waals heterostructures formed by molecular assemblies and 2D materials provide a novel platform for fundamental nanoscience and future nanoelectronics applications. A prototypical hybrid heterostructure between pentacene molecules and 2D MoS_2 nanocrystals was prepared by deposition on Au(111) and characterized both experimentally and computationally. The defective nature of the MoS_2/Au interface,[1] and the simulation of pentacene adsorption[2] reveal intriguing structural, physical and chemical properties.

N-Heterocyclic Carbenes (NHCs) and olefins (NHOs) are prone to form strong chemical bonds on metal surfaces, thanks to their pronounced electron-donor character, which enables their use in surface functionalization for various applications, from gas sensing to optoelectronics and (photo)catalysis. We went beyond the paradigmatic case of Au(111), widely studied in the literature, to investigate NHCs and NHOs adsorption, diffusion, and assembly on copper and copper oxide surfaces.[3-5]

[1] Tumino et al., *Nature of Point Defects in Single-Layer MoS_2 Supported on Au(111)*, J. Phys. Chem. C **2020**, *124*, 12424

[2] Tumino et al., *Interface-Driven Assembly of Pentacene/MoS_2 Lateral Heterostructures*, J. Phys. Chem. C **2022**, *126*, 1132

[3] Navarro et al., *Growth of N-heterocyclic carbene assemblies on Cu (100) and Cu (111): from single molecules to magic-number slands*, Angew. Chem.-Int. Edit. **2022**, 30, e202202127

[4] Navarro et al., *Covalent adsorption of N-heterocyclic carbenes on a copper oxide surface*, J. Am. Chem. Soc. **2022**, 144, 16267

[5] Landwehr et al., *N-Heterocyclic Olefins on Cu(111)- Adsorption, Orientation and Electronic Influence*, **2023**, submitted