Activation Mechanisms of layered MoS_2 Surfaces probed by time-based and time-resolved Electron Spectroscopy

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Layered transition metal dichalcogenides such as molybdenum disulphide (MoS_2) have widely tunable properties making them relevant for electronics, sensors, energy storage, and catalysis. For MoS_2 we have thus investigated the inhomogeneity and homogenization of the local n- and p- doping character of bulk MoS_2. In particular, a cleaved surface typically displays spatially inhomogeneous properties. Annealing and exposure to molecular hydrogen can be cycled to switch reversibly between smaller and larger surface band bending preserving local inhomogeneity. Atomic hydrogen exposure, however, equilibrates reversibly the entire surface to a common doping situation due to the amphoteric effect of hydrogen atoms to serve as donors and acceptors alike, neutralizing local charge imbalances.[1] Optical excitation is shown to create a transient metallic surface layer on bulk semiconducting MoS_2 where electrons in the conduction band of p-doped semiconducting MoS_2 travel toward the surface layer.[2] They accumulate in the top layer and create a transient reversible 2H-semiconductor to 1T-metal phase-transition of the surface layer. Electron–phonon coupling of the indirect-bandgap p-doped 2H-MoS_2 enables this efficient pathway even at a low density of excited electrons with a distinct optical excitation threshold and saturation behavior. This mechanism needs to be taken into consideration when describing the photocatalytic properties of the 2H-MoS_2 surface. In particular, light-induced increased charge mobility and surface activation can cause and enhance the photocatalytic and photo assisted electrochemical hydrogen evolution reaction of water on 2H-MoS_2. Generally, it opens up for a way to control not only the surface of p-doped 2H-MoS_2 but also related dichalcogenides and layered systems.[2] All findings are based on time based and time resolved electron spectroscopy for chemical analysis with photon-energy-tunable synchrotron radiation.

Keywords: Dichalcogenide, Surface Activation, Phase Transition, Intercalation, Doping, Amphoteric Effect of Hydrogen, Photoelectrocatalysis. Electron Spectroscopy

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[1] E. Giangrisostomi, et al, Inhomogeneity of Cleaved Bulk MoS_2 and Compensation of Its Charge Imbalances by Room-Temperature Hydrogen Treatment. *Mater. Interfaces* **10**, 2300392 (2023).

[2] N.L.A.N. Sorgenfrei et al. Photodriven Transient Picosecond Top-Layer Semiconductor to Metal Phase-Transition in p-Doped Molybdenum Disulfide. *Adv. Mater.* **33**, 2006957 (2021).