Monolayers of α-MoO$_{3-x}$ on graphite substrate – growth and electronic structure characterization

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Molybdenum oxides play an important role in many applications, ranging from catalysis, batteries, and gas sensors to optoelectronics. With the on-going desire for flexible organic electronics, efforts are actively taken towards graphene-based electrodes addressing, in particular, devices with MoO$_3$ as a hole injection layer (HIL). The practical attractiveness of α-MoO$_3$ has been enhanced by theoretical predictions that the electronic structure of 2D α-MoO$_3$ is not significantly altered from the bulk.

The unit cell of α-MoO$_3$ contains two layers of chemically bonded octahedra separated by a van der Waals gap. Here we define a monolayer (1L) of MoO$_3$ as a single layer of the octahedral net, which corresponds to half of the unit cell with the thickness of 6.9 Å. In contrast to previously available results, we present highly stable 1L α-MoO$_{3-x}$ which uniformly covers the graphite (HOPG) substrate [1]. We chose such substrate to analyze the growth process on a near perfect, defect- and contamination-free graphene-like layer. This allows for precise scanning probe microscopy characterization performed under the UHV conditions and gives the direct information about fundamental physical properties essential for further organic electronic applications.

We prove that van der Waals epitaxy performed by thermal evaporation under UHV is efficient to synthesize the 2D, non-stoichiometric, and electrically conductive MoO$_{3-x}$. By a combination of ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS), we investigate the chemical composition of α-MoO$_{3-x}$ /HOPG and the interface-induced defects states. Using scanning tunnelling microscopy and spectroscopy, we investigate the electronic properties of MoO$_{3-x}$ as a function of the number of layers and measure the apparent energy gap to be 0.4 eV for the first three layers of MoO$_{3-x}$ on graphite. Additionally, we carry out density functional theory calculations to shed light on the mechanism underlying the observed narrow bandgap with oxygen deficiency.

Our results provide insight on the heterogeneity of 1L MoO$_{3-x}$ at the interface with the graphene-like substrate and can contribute to fundamental understanding of the interfacial 1L-MoO$_{3-x}$ /graphene electronic structure.
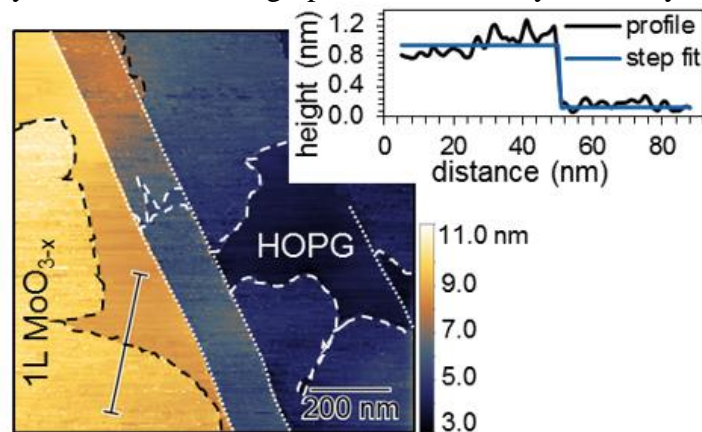
[1] D.A. Kowalczyk, M. Rogala, K. Szałowski, *et al.*, 2D Materials **8**, 025005 (2021).