

# WO<sub>3</sub> Monolayer on Pd(100): An Advanced Model Catalyst for Reactivity Studies

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Tungsten oxide (WO<sub>3</sub>) is a key material in several applications including smart windows technology, photo-electrochemical water splitting, gas sensors and heterogeneous catalysis. In particular, tungsten oxides are important acid-base and redox catalysts, and they show excellent activity for many catalytic reactions, such as alcohol dehydrogenation, alkane hydrogenation and metathesis [1]. WO<sub>3</sub> has been produced in single crystal form or as supported thin films with the bulk crystal structure. The latter is strongly temperature dependent, displaying a series of polymorphs, based on an idealized cubic ReO<sub>3</sub> corner-sharing WO<sub>6</sub> octahedral framework. Recently, the formation of an ordered two-dimensional (2D) tungsten oxide layer on Pt(111) has been reported, where however W atoms show a mixture of 5+ and 6+ oxidation states [2]. In principle, 2D oxide films may be regarded as so-called “oxide monolayer catalysts”, since they may exhibit higher catalytic activities for selective oxidation reactions than their bulk counterparts [3].

Here we report on the preparation of a well-ordered 2D WO<sub>3</sub> layer on a Pd(100) surface and the characterization of its geometric, electronic and vibrational structure by a combination of STM, LEED, XPS and HREELS. The WO<sub>3</sub> monolayer wets completely the Pd(100) surface (Fig. 1a) and features a surface network consisting of small (~ 4 nm) square-shaped domains, separated by narrow (~ 0.5 nm) trenches. The latter are identified as anti-phase domain boundaries, as evidenced by atomically-resolved STM images (see inset of Fig. 1a) and the characteristic spot splitting around the ( $\pm 1/2$ ,  $\pm 1/2$ ) LEED positions (Fig. 1b). The STM image shows that each domain exhibits a square surface structure with a lattice constant of 0.39 nm, which corresponds to a c(2x2) superstructure. Another important feature is the presence of few dark depressions inside the domains, which we attribute to missing terminal O atoms (see model in Fig. 1d), in corroboration with HREELS results and high-resolution W 4f core-level spectra (Fig. 1c). The latter consist of three 4f<sub>7/2</sub> - 4f<sub>5/2</sub> doublet components, due to W atoms at different surface locations: within the defect-free areas (major component at 34.4 eV), with missing terminal oxygens (minor component at 33.3 eV), and at the domain boundaries (35.2 eV). The proposed structure model of the WO<sub>3</sub> monolayer is shown in Fig. 1d and consists of a layer of O atoms adsorbed in fourfold hollow Pd positions, followed by a c(2x2) layer of W atoms, which are connected at the top to terminal O atoms via strong W=O bonds, as suggested by our HREELS results. It can be viewed in a way as a 2D analogue of a cubic WO<sub>3</sub>(001) crystal, featuring a similar lattice constant (0.39 nm vs. 0.38 nm) and polyhedral linkage, but with a modified W-O coordination sphere due to the contact with the Pd(100) surface. We consider this 2D WO<sub>3</sub> layer on Pd(100) as a well-defined monolayer model catalyst, which can be potentially suitable for reactivity studies.

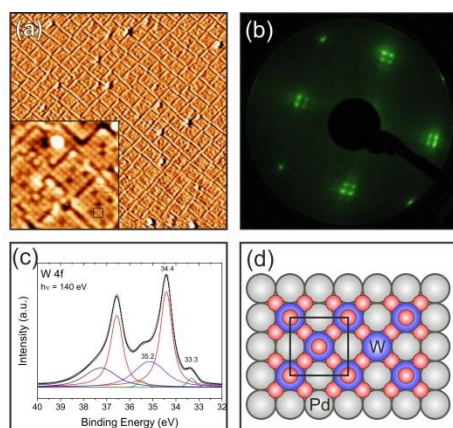


Fig. 1: (a) STM image (65nm x 65nm) of the WO<sub>3</sub> monolayer on Pd(100). The inset displays a high-resolution STM image (8.5nm x 8.5nm) of the 2D WO<sub>3</sub> phase (the c(2x2) unit cell is indicated); (b) LEED pattern, showing the spot splitting due to anti-phase domain boundaries; (c) High-resolution W 4f spectrum of the WO<sub>3</sub> monolayer, decomposed into three different components, as discussed in the text; (d) Proposed structure model of the 2D WO<sub>3</sub> layer on Pd(100), the c(2x2) unit cell is indicated (Pd: gray; W: blue; O: red).

[1] D. Gazzoli et al, J. Phys. Chem. B 101 (1997) 11129

[2] Z. Li, et al, J. Phys. Chem. C 115 (2011) 5773

[3] G. Deo, et al, Crit. Rev. Surf. Chem. 4 (1994) 141

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