

Oxide honeycomb monolayers: Ti_2O_3 and Nb_2O_3 (2×2) on Au(111)

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Two-dimensional transition metal oxides (TMOs) supported on metal substrates form an exciting class of materials with potential applications in catalysis, electronics, and energy storage [1]. Due to the strong epitaxial interaction between metal substrates and TMO films, many of the observed lattices are unique and only exist in two dimensions. A subset of TMOs crystallize into a honeycomb (2×2) monolayer; for example V_2O_3 on Pd(111) [2] and $\text{Ti}_2\text{O}_3/\text{Nb}_2\text{O}_3$ on Au(111) [3,4].

We report the experimental characterisation and theoretical analysis of epitaxial (2×2) honeycomb Nb_2O_3 and Ti_2O_3 monolayers on an Au(111) substrate. The oxide monolayers are grown by Nb/Ti deposition and subsequent annealing in an oxidizing atmosphere. Scanning tunnelling microscopy (STM) images show that the films form a well-ordered honeycomb lattice, and low energy electron diffraction patterns confirm that the films adopt a (2×2) periodicity with respect to the Au(111) substrate. Density functional theory (DFT) modelling shows that the Nb/Ti atoms are located in Au(111) threefold hollow sites and the O atoms are located in on-top positions. DFT also demonstrates the existence of a strong interfacial interaction characterized by a large electron transfer towards the Au substrate, an increase of the Nb/Ti oxidation state, and substantial film rumpling.

In the perfect Nb_2O_3 lattice, the Nb atoms are 3-fold coordinated with respect to O, however, at defect sites the Nb can become 4-fold coordinated. This 4-fold coordination is not observed in similar Ti_2O_3 monolayers on Au(111) due to the smaller number of valence electrons. Four-fold coordinated niobium atoms are stable in a host of different configurations such as multiple vacancy structures, line defects, domain boundaries, and edge reconstructions. Recent calculations have demonstrated that an important contribution to the stability and effective formation of ternary TMOs on metal supports is the ability of the cations to adopt different oxidation states [5]. The on-surface redox capability of niobium, as evidenced by these four-fold coordinated motifs seems to be a decisive characteristic for their incorporation in more complex ternary structures.

1. "Oxide Materials at the Two-Dimensional Limit" by Netzer and Fortunelli (Eds.).
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3. Wu et al., *J. Phys. Chem. C*, **115**, 8643 (2011)
4. Wang et al., *Phys. Rev. B*, **100**, 125408 (2019)
5. Goniakowski et al., *J. Phys. Chem. C*, **124**, 8186 (2020)