

**FISRT STAGES OF THE GROWTH OF PT-CLUSTERS ON QUASI-METALLIC 1D ROWS OF TiO<sub>2</sub>(110)-(1X2) SURFACES.**

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The surface of metal oxide materials is of huge technological relevance in a wide variety of fields, ranging from catalysis to fundamental chemistry. Although the rutile TiO<sub>2</sub>(110) surface has been extensively studied, the intrinsic difficulties, associated to defects and *history* of the sample, has lead to a limited basic knowledge on these materials. This is particularly true for the non-stoichiometric (1x2) reconstruction formed after reducing the surface by annealing up to about 800°C. This reconstruction, although widely studied, presents a large variety of defects, which rends the understanding of its basic properties, still nowadays, unclear. Several models have been proposed to date, but they differ even in the stoichiometry [1,2]. Combining STM, quantitative LEED, Angle resolved ultraviolet photoemission spectroscopy (ARUPS) and density functional theory (DFT), we have determined the atomic surface structure and electronic properties of rutile TiO<sub>2</sub>(110)-(1x2). STM images show monoatomic steps, wide terraces and no cross-link features. The most suitable model to explain them consists of added Ti<sub>2</sub>O<sub>3</sub> rows along the [001] direction [2]. A more detailed LEED-IV analysis, using a large database of intensities, recorded both normal and off-normal incidences, yields the relaxed surface parameters with a Pendry R-factor  $R_p = 0.29$ . Atomic coordinates are in good agreement with the minimum energy structure provided by DFT. Discrepancies can be explained by the large thermal vibration amplitudes found for the Ti<sub>2</sub>O<sub>3</sub> group[2].

Surprisingly, the electronic structure derived from DFT shows a metallic character along the [001] direction. This striking feature is evidenced by parabollic dispersion bands crossing the Fermi level along the [001] direction, whereas in the perpendicular direction bands are rather flat [1]. The long quasi-1D chains display metallic character, do not show any interaction between them, and cannot couple to bulk or surface states in the gap region, forming good one-dimensional atomic wires. These electronic bands cannot be found in ARUPS because they are very close to the Fermi edge and disperse upwards, towards the conduction band. STM images show the presence of defect-free atomic chains covering all

terraces from one monoatomic step to the next. STS current-voltage curves, which reflect the local DOS, show qualitative agreement with UPS spectra.

On this deeply atomic and electronically characterized surface, we have deposited Pt at submonolayer coverages. The idea behind is that the catalytic properties of the surface could be enhanced due to the larger  $\text{Ti}_2\text{O}_3$  conductivity. We have followed the first stages of adsorption from the first arriving adatoms to the cluster formation at about 1 ML. The ridges between  $\text{Ti}_2\text{O}_3$  rows appear by DFT as the most favorable adsorption sites, making easier the formation of 1D structures. The growth process has been followed by angle resolved UPS and STM, gathering a picture of the main growth mechanisms.

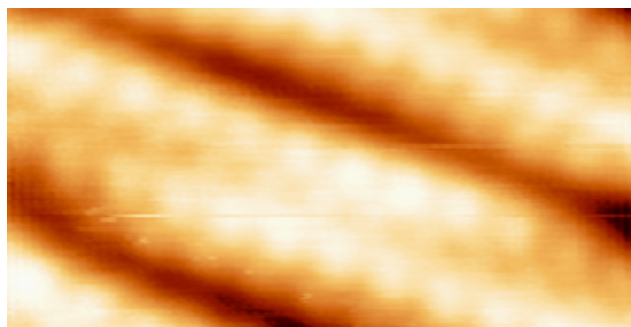
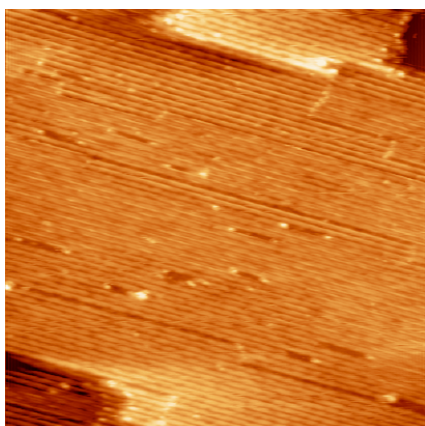
Summarizing, by a combination of different experimental techniques and theoretical methods we have characterized the atomic structure and the electronic properties of the  $1 \times 2$  reconstructed  $\text{TiO}_2(110)$  surface, which consist of quasi-1D metallic chains with a  $\text{Ti}_2\text{O}_3$  stoichiometry. On these chains we have deposited and characterized, both atomic and electronically, submonolayers of Pt which evolves from low-dimensional features to metallic clusters

### References:

[1] M. Blanco-Rey, J. Abad, C. Rogero, J. Mendez, M. F. Lopez, J. A. Martin- Gago, P. L. de Andres, Phys. Rev. Lett. **96** (2006) 055502.

[2].- M. Blanco-Rey, J. Abad, C. Rogero, J. Mendez, M. F. Lopez, E. Roman, J. A. Martin-Gago, P. L. de Andres, Phys Rev.B, **75** (2007) 081402(R).

### Figures:



**Left:** Typical STM image of the  $1 \times 2$  reconstruction of the  $\text{TiO}_2(110)$ , showing large chains running continuously along the  $[001]$  surface direction. The total width of the image is  $100 \times 100 \text{ nm}^2$ . **Right:** Typical atomic resolved STM image of the  $1 \times 2$  reconstruction of the  $\text{TiO}_2(110)$ . The total width of the image is  $4 \times 2.7 \text{ nm}^2$ .