

Measurement and manipulation of the charge state of oxygen adatoms on $\text{TiO}_2(110)$ surface by atomic force microscopy

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Oxygen-rich $\text{TiO}_2(110)$ surface has attracted a lot of research interest due to playing the important role in catalytic oxidation reactions, and many works have focused on the adsorption and dissociation of oxygen molecules on $\text{TiO}_2(110)$ surface [1][2]. Up to now, two adsorption and dissociation channels of oxygen molecules on $\text{TiO}_2(110)$ were observed by scanning tunneling microscopy (STM), namely, the oxygen vacancy (O_v) assisted and the transversely-aligned adsorption and dissociation on five-fold coordinated Ti site (Ti_{5c}) [3]. Actually, the charge state of the oxygen adatoms adsorbed on the $\text{TiO}_2(110)$ surface is important to clarify the mechanism of catalytic reactions, and has not been investigated. In this study, the charge state of the oxygen adatoms was measured and manipulated by non-contact atomic force microscopy (NC-AFM) and Kelvin probe force microscopy (KPFM).

In the experiment, the home-built NC-AFM and KPFM with bias voltage feedback were employed. The oxygen was exposed at the low temperature (78 K). In order to remove the crosstalk of the surface topography, the local contact potential difference (LCPD) and frequency shift (Δf) images were obtained at the constant height mode. We measured and manipulated the charge state of the oxygen adatoms adsorbed on the $\text{TiO}_2(110)$ surface under ultrahigh-vacuum condition at 78 K. Based on the experimental results, two kinds of charge state of the oxygen adatoms were observed, namely, the super-oxo (O_a^{1-}) and peroxy (O_a^{2-}) oxygen adatoms, which could be obviously distinguished in the AFM, LCPD and Δf images. Fig. 1 (a) shows the NC-AFM image of the oxygen-rich $\text{TiO}_2(110)$ surface and the cross-section line profiles of single and double oxygen adatoms with super-oxo and peroxy charge state as well as the charged oxygen molecule (O_2^-) are shown in Fig. 1 (b) and (c). In addition, the charge state of the oxygen adatoms can be deliberately switched between super-oxo and peroxy state, which is driven by the tip-induced local electric field between the AFM tip and sample surface [4]. The magnitude of the electrical field can be controlled by the tip-sample distance and the bias voltage applied to the sample. This work can provide a valuable reference for the research of catalytic oxidation reactions.

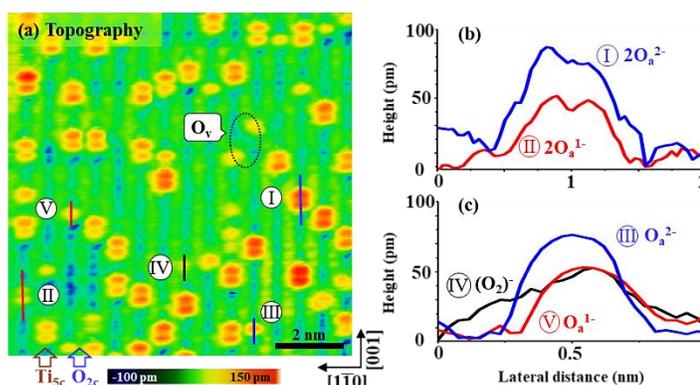


Fig. 1: (a) NC-AFM image of the oxygen-rich $\text{TiO}_2(110)$ surface. (b) and (c), the cross-section line profiles of single and double oxygen adatoms with super-oxo and peroxy charge state as well as the charged oxygen molecule.

References

- [1] D. Yingge *et al.* *Phys. Chem. Chem. Phys.* **12**, 6337-6344 (2010).
- [2] L. Estephania *et al.* *Surface Science* **604**, 1945-1960 (2010).
- [3] M. Jesper *et al.* *ACS Nano* **3**, 517-526 (2009).
- [4] N. Kocić *et al.* *Nano Lett.* **15**, 4406-4411 (2016).