Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Imaging Oxygen Molecular Adsorption and Dissociation on the Ti Site of Rutile TiO_2(110) Surface with Real Configuration at 78 K by Atomic Force Microscopy

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Table S1. Reorientation energy (energy differences between the end-on and side-on geometries) under the influence of electric field generated by STM tip, calculated using PBE0-TC-LRC-ADMM hybrid density functionals[1,2] implemented within code CP2K[3].

Electric Field (V/Å)	-0.5	-0.1	0	0.1	0.5
Reorientation Energy[a] (eV)	0.736	0.690	0.654	0.647	0.455
Reorientation Energy[b] (eV)	unstable	1.413	1.365	1.256	0.854

The system is charged with (a) one or (b) two extra electrons. Side-on geometry is energetic more stable at all charge states, and the energy penalty in the configuration transition from side-on to end-on is significantly smaller with one extra electron compare to two electrons. Hence, the population of end-on is expected to be more noticeable when the system is singly charged.

1. M. Guidon, J. Hutter, and J. VandeVondele, Robust Periodic Hartree-Fock Exchange for Large-Scale Simulations Using Gaussian Basis Sets, J. Chem. Theory Comput. 5, 3010-3021 (2009).
2. M. Guidon, J. Hutter, and J. VandeVondele, Auxiliary Density Matrix Methods for Hartree-Fock Exchange Calculations, J. Chem. Theory Comput. 6, 2348-2364 (2010).
3. J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, and J. Hutter, QUICKSTEP: Fast and Accurate Density Functional Calculations Using a Mixed Gaussian and Plane Wave Approach, Comput. Phys. Commun. 167, 103-128 (2005).

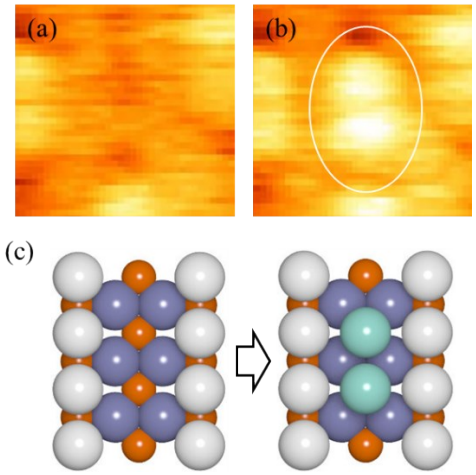

Figure S1. AFM images (a) before O_2 adsorption, (b) after O_2 dissociation and (c) corresponding structural models on TiO_2(110) surface. (f_0 = 801 kHz, Q = 19727, Δf = -362 Hz, V_S = 1 V, A = 500 pm, 1.3×1.3 nm^2)

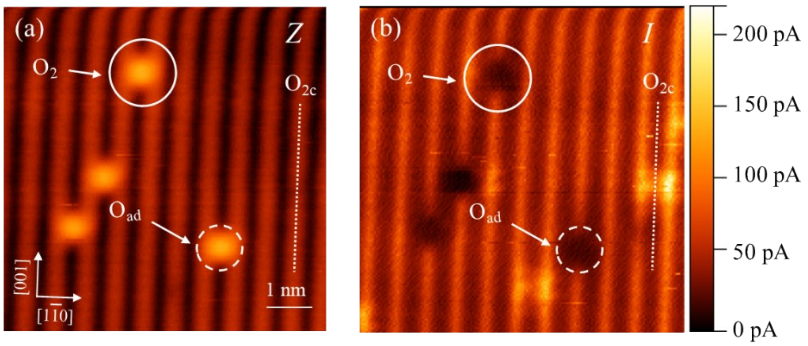

Figure S2. Simultaneously recorded (a) topographic images and (b) tunneling current image performed in the constant frequency shift mode.

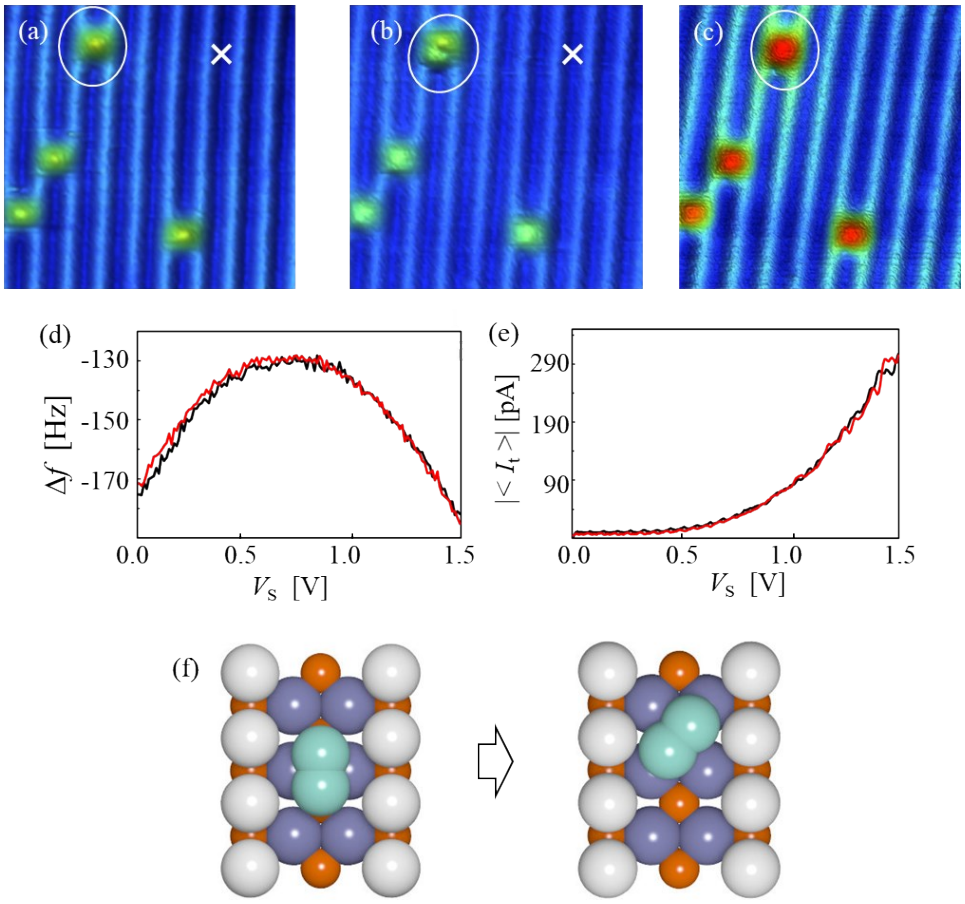

Figure S3. (a)-(c) The transition between the bright spot and two weak bright spots with inclined side-on configuration induced by KPFS. (d)-(e) KPFS is performed on the cross site in (a)-(b). (f) The corresponding structural models. The bright spot marked by white elliptical circle can be assigned to paralleled side-on configuration.

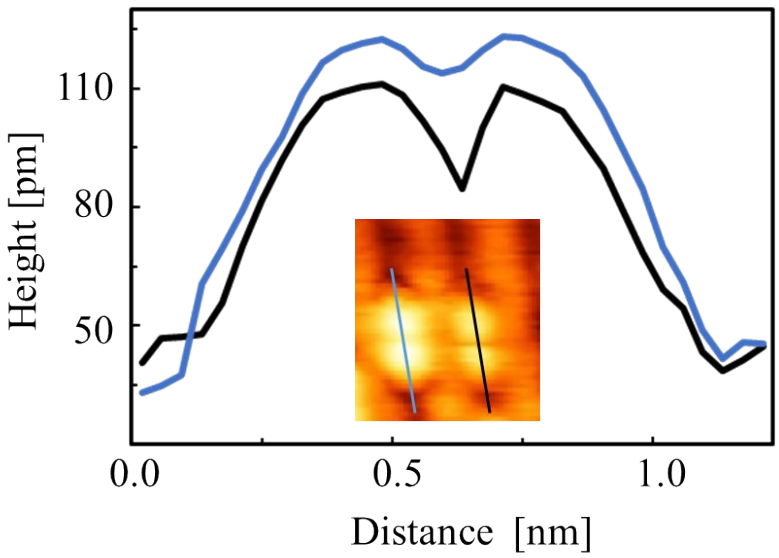

Figure S4. Line profiles along the different charge state of O_{ad} from Figure 1