## Trapping Nitric Oxide by Surface Hydroxyls on Rutile $TiO_2(110)$

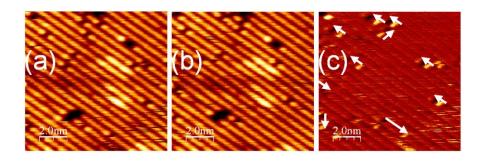
Shao-Chun Li, †,‡,\* Peter Jacobson, †, § Shu-Lei Zhao, "Xue-Qing Gong," and Ulrike Diebold †, §,\*

<sup>†</sup>Department of Physics and Engineering Physics, Tulane University, New Orleans, LA 70118, U.S.A. <sup>‡</sup>National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, P. R. China

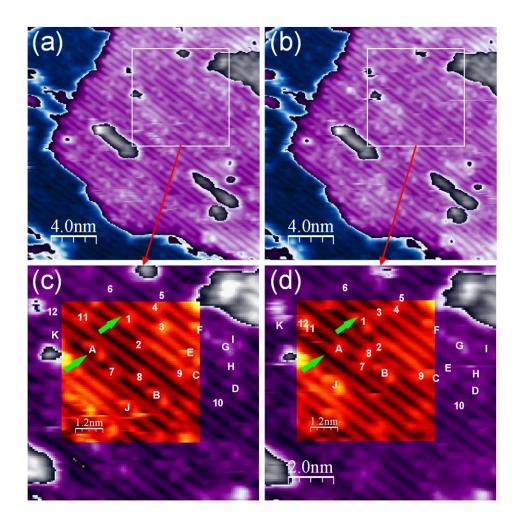
§Institute of Applied Physics, Vienna University of Technology, Wiedner Hauptstrasse 8-10/134, 1040 Vienna, Austria

State Key Laboratory of Chemical Engineering, Centre for Computational Chemistry and Research Institute of Industrial Catalysis, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China

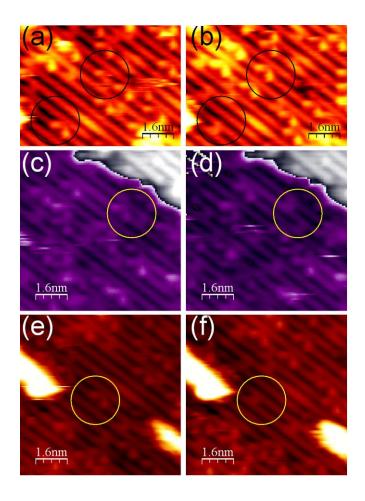
<sup>\*</sup> Email: shaochun.li.stm@gmail.com; diebold@jap.tuwien.ac.at



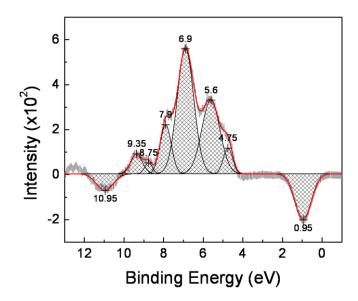
**Figure S1.** (a, b) Two consecutive STM images ( $10 \text{ nm} \times 10 \text{ nm}$ , I = 0.2 A, V = +1.7 V), take with time interval of 2 min. (c) Difference image obtained by subtracting (a) from (b). White arrows show the motion of the NO-related adsorbate.



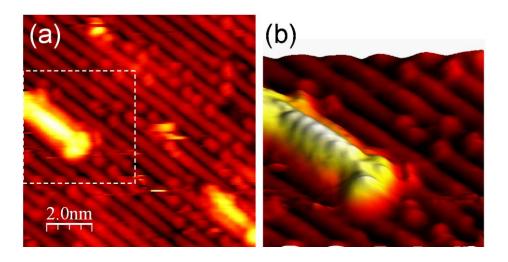
**Figure S2.** (a, b) Large-area scans corresponding to the STM images shown in Figure 2a and 2b in the main text. (c,d) Zoom-in images of the selected area in (a,b). The area displayed in Figure 2a and 2b is shown in red-color scale; the rest of the images are displayed in purple/gray scale. Letters A to K mark the NO-related adsorbates and numbers 1 to 12 hydroxyls. Each hydroxyl and NO-related feature is accounted for in both images, except for "A" and "1", which represent a disappeared NO-related adsorbate and an appeared hydroxyl, respectively. Movie S1 is composed of images (c) and (d), and shows how the tracking of these adsorbates are performed.



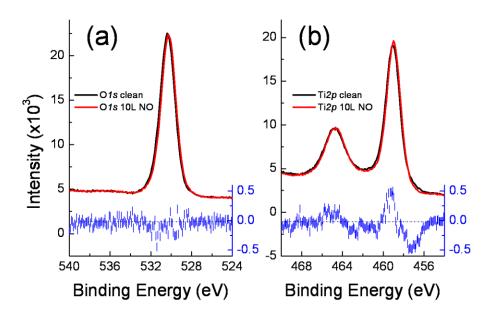
**Figure S3.** Three examples of simultaneous ad/desorption of an NO-related complex and an OH group. The time interval between two consecutive images is 2 min.  $V_{\text{sample}} = +1.6V$  and  $I_{\text{tunnel}} = 0.2 \text{ nA}$ 



**Figure S4.** The difference spectrum from Figure 2a. Negative values represents peaks that are decreased upon NO adsorption (i.e., the Ti3+ state at 0.9 eV and the OH  $3\sigma$  state at 10.9 eV). The positive values show states that appear in the valence band upon NO exposure, these are fitted with six Gaussians.



**Figure S5.** (a) STM image ( $10 \text{ nm} \times 10 \text{ nm}$ ) showing a  $Ti_2O_3$  strip and NO-related adsorbates. (b) 3D rendering of the white square area in (a).



**Figure S6.** O*Is* (a) and Ti 2p (b) X-ray photoemission spectra of a hydroxylated TiO<sub>2</sub>(110) surface (black) and the surface after dosing NO (red). The blue scatter plots were obtained by subtracting the clean from the NO-exposed spectrum after aligning the peaks in each case.