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\textsuperscript{1,2} implemented within code CP2K\textsuperscript{3}.

<table>
<thead>
<tr>
<th>Electric Field (V/Å)</th>
<th>-0.5</th>
<th>-0.1</th>
<th>0</th>
<th>0.1</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reorientation Energy\textsuperscript{a} (eV)</td>
<td>0.736</td>
<td>0.690</td>
<td>0.654</td>
<td>0.647</td>
<td>0.455</td>
</tr>
<tr>
<td>Reorientation Energy\textsuperscript{b} (eV)</td>
<td>unstable</td>
<td>1.413</td>
<td>1.365</td>
<td>1.256</td>
<td>0.854</td>
</tr>
</tbody>
</table>

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.

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, $Q = 19727$, $\Delta f = -362$ Hz, $V_S = 1$ V, $A = 500$ pm, $1.3 \times 1.3$ 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