Supporting Information

Formation of O adatom pairs and charge transfer upon O_2 dissociation on reduced $TiO_2(110)$

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S1: STM movie (S1.avi) of the (25×25) nm^2 area of TiO$_2$(110) surface taken during ~80 min of O$_2$ dosing, with an acquisition time of 126 s per frame. More than 160 O$_2$ dissociation events resulted in O vacancy, V$_O$, healing and depositing single O adatoms, O$_a$, and also the appearance of O$_a$-O$_a$ pairs, all have been recorded. (The sample had an initial V$_O$ concentration of 0.12 ML).
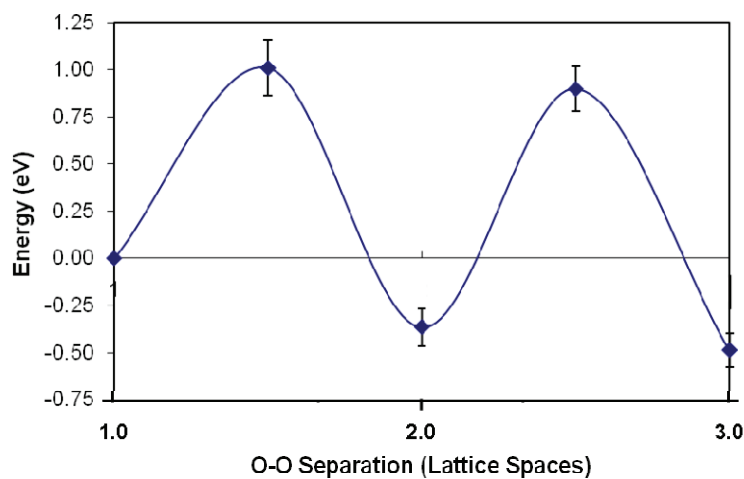
Figure S2. Average relative energies for O_a-O_a pairs separated by one, two, or three lattice spaces away. The configuration with the O_a-O_a pair separated by one lattice site is taken as 0 eV. The results have been averaged over many different configuraitons, where the V_O locations within the 6×2 supercell have been varied relative to the O_a. The error bars indicate the standard deviation from the averaged results.

S3: Modeling

S3.1 Scenario 1 (total formal charge can be withdrawn from a V_O)

V – Initial coverage of V_O's
O_1 – Coverage of single O_a's in the presence of only V_O's (no Ti interstitials)
O_2 – Coverage of paired O_a's in the presence of only V_O's
$\tilde{\delta}$ – Effective charge of an O_a

Since each V_O has nominally two unpaired electrons, then in the presence of only V_O's (no Ti interstitials) the full surface charge available to facilitate O_2 dissociation is $V2e^-$.

The O_2 molecules dissociate at both V_O and terminal Ti sites. Complete charge withdrawn from V_O's upon O_2 dissociation at V_O sites, which results in one annihilated V_O and one O_a formation, is $O_1(2e^- + \tilde{\delta})$. Complete charge withdrawn from V_O's upon O_2 dissociation at Ti sites, which results in O_a-O_a pair formation, is $O_2\tilde{\delta}$. Accordingly, full charge withdrawn from V_O's upon O_2 dissociation is $O_1(2e^- + \tilde{\delta}) + 2O_2\tilde{\delta}$.

Then, charge balance in the presence of only V_O's can be written as:

$$(1) \qquad V2e^- = O_1(2e^- + \tilde{\delta}) + O_2\tilde{\delta}$$

The ratio between paired and single O_a's of ~ 0.6 (0.036/0.059) has been estimated from experimental data in Figure 6 (whereby presumably both V_O and Ti interstitials could provide charge). Since it is reasonable to expect that reaction rates for O_2 dissociation either at V_O or Ti sites do not depend much on the source of extra charge (V_O's or Ti interstitials), we assume that the ratio between paired and single O_a's in the presence of only V_O's (no Ti interstitials), O_2/O_1, is about the same (0.6).

Then, for a case where $\tilde{\delta} = 2e^-$ (a full formal charge), the total O_a number can be deduced from the initial V_O coverage (0.12 ML) using equation (1), as 0.074 ML.

For a case where $\tilde{\delta} = 0.7e^-$ (a Bader charge), $O_2 + O_1$ is ~ 0.11 ML.

S3.2 Scenario 2 (only a fraction of charge can be withdrawn from a V_O)

V_u – Saturation coverage of V_O's left unfilled
O_a – Saturation coverage of O_a's attributed to V_O's
$\tilde{\delta}$ – Effective charge of an O_a
δ_V^- – Charge withdrawn from a V_O

Maximum charge transferred to O_a's from V_O's can be written as:

$$(2) \qquad O_a\delta = V_u\delta_V^-$$

The recent STM studies indicate that all bridging hydroxyls can be removed from a fully hydroxylated TiO_2(110) by reaction with O_2.[1,2] If all the available charge would be provided by V_O's, the reaction would terminate after full oxidation of the surface is

reached. Nonetheless, the formation of O containing species on Ti rows has been observed after further O_2 exposure, with a saturation coverage of ~ 40% of original V_O concentration, indicating a presence of additional charge (likely Ti interstitial related) that mediates further O_2 dissociation.[3] In our case with initial V_O coverage of 0.12 ML, it will correspond to 0.048 ML of O_a's attributed to Ti interstitial. Thus, O_a (saturation coverage of O_a's attributed to V_O's) is 0.047 ML out of 0.095 ML (saturation coverage for O_a's projected from the experimental data, Figure 6). Further, after taking into account the coverage of unfilled V_O's (V_u = 0.06 ML, Figure 6), one can estimate the average amount of charge donated by each V_O.

For a limiting case where $\tilde{\delta} = 2e^-$ (a full formal charge) and using equation (2), δ_{V}^- is found to be ~ $1.6e^-$.

For a case where $\tilde{\delta} = 0.7e^-$ (a Bader charge), δ_{V}^- is ~ $0.5e^-$.

References

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(3) Petrik, N. G.; Zhang, Z. R.; Du, Y. G.; Dohnalek, Z.; Lyubinetsky, I.; Kimmel, G.A. *J. Phys. Chem. C* **2009**, *113*, 12407.