

Supplementary Information

for

Subtle Structure Matters: Boosting Surface-directed Photoelectron Transfer via the Introduction of Specific Monovalent Oxygen Vacancies in TiO₂

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1. Supplementary results

Table S1. Two examples (shown as Figure 2a and Figure 4c (III-IV) in the article) for comparing difference in calculated energy changes (energy unit: eV) by the PBE+U and HSE06 single-point methods.

Method	Figure 2a	Figure 4c (III-IV)
PBE+U	-0.37	-0.02
HSE06	-0.34	-0.01

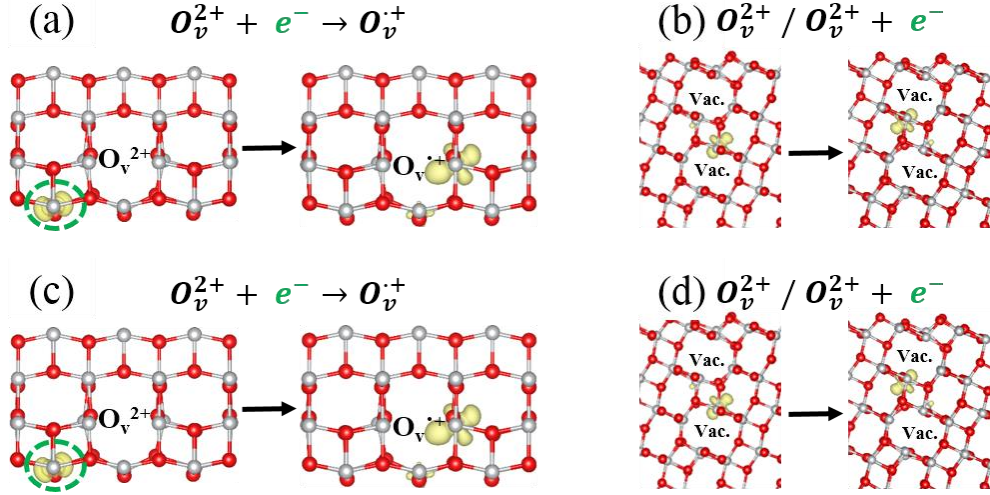


Figure S1. Calculated structures and spin-polarized charge densities (iso-value of 0.008 $|e|/\text{Bohr}^3$) of two examples (shown as (a, c) Figure 2a and (b, d) Figure 4c (III-IV) in the manuscript) obtained using (a, b) PBE+U and (c, d) HSE06 single-point methods.

Table S2. Calculated energy change (ΔE) of an additional electron migrating from bulk Ti_{6c} to surface Ti_{5c} in two anatase TiO_2 slabs containing five and eight Ti-layers, respectively. We considered two approaches for simulating an additional electron: i) adding one electron via setting the NELECT parameter in the VASP; ii) introducing a H atom on the opposite surface of TiO_2 slab, which produces a protonated O_{2c} and an additional electron trapped at a specific Ti ion.

$\Delta E / \text{eV}$	Introducing 1 e^-	Introducing 1 H
5-Ti-layer $p(2 \times 4)$ slab	-0.08	0.00
8-Ti-layer $p(2 \times 3)$ slab	-0.05	0.02

Table S3. Calculated energy change (ΔE) of an additional electron migrating from a bulk O_v^{2+} to anatase $\text{TiO}_2(101)$ surface. We considered two approaches for removing an electron: i) setting the NELECT parameter in the VASP; ii) introducing a OH group on the opposite surface of TiO_2 slab, which captures an electron and turns into OH^- ions.

$\Delta E / \text{eV}$	Removing 1 e^-	Introducing 1 OH
5-Ti-layer $p(2 \times 4)$ slab	0.11	0.06
8-Ti-layer $p(2 \times 3)$ slab	0.15	0.11

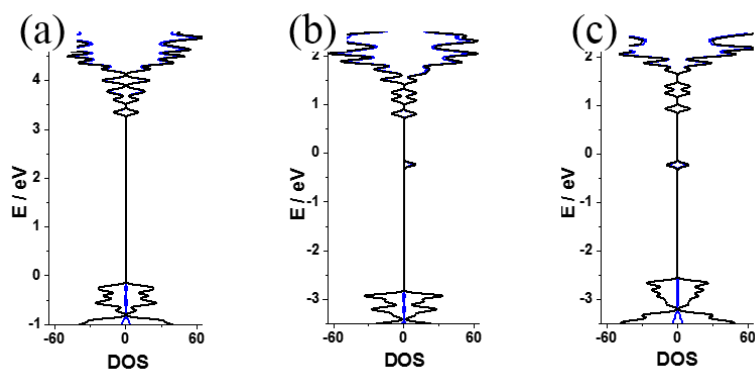


Figure S2. Calculated electronic total DOSs (black lines) and Ti 3d PDOSs (blue lines) of (a) divalent O_v^{2+} , (b) monovalent O_v^{+} , and (c) neutral O_v^{\cdot} in bulk anatase TiO_2 . The position of the Fermi Level is aligned at zero in energy coordinate.

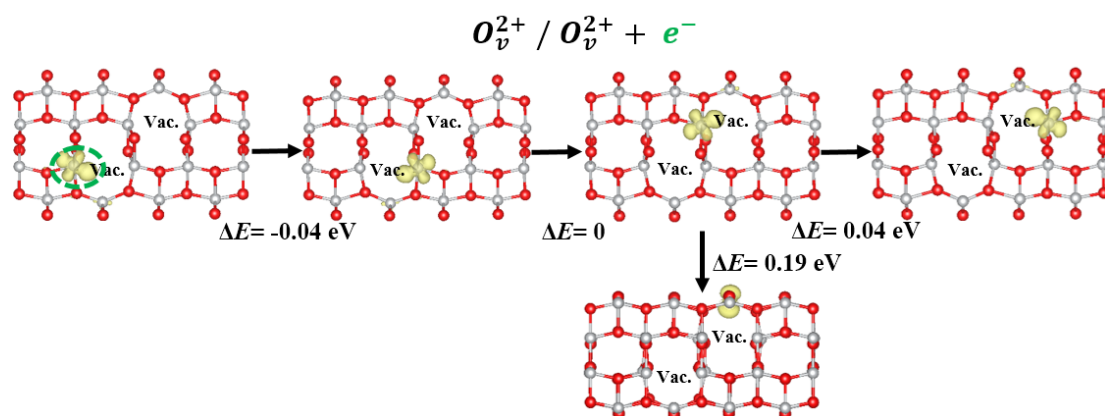


Figure S3. Calculated charge densities (iso-value of $0.005 |e|/\text{Bohr}^3$) and energies (ΔE) of an additional electron (indicated by green circles) migrating along the O_v^{2+} chain in bulk anatase TiO_2 . The energy cost of electron deviation from symmetric Ti_{5c} to the odd one is presented in the lower panel.

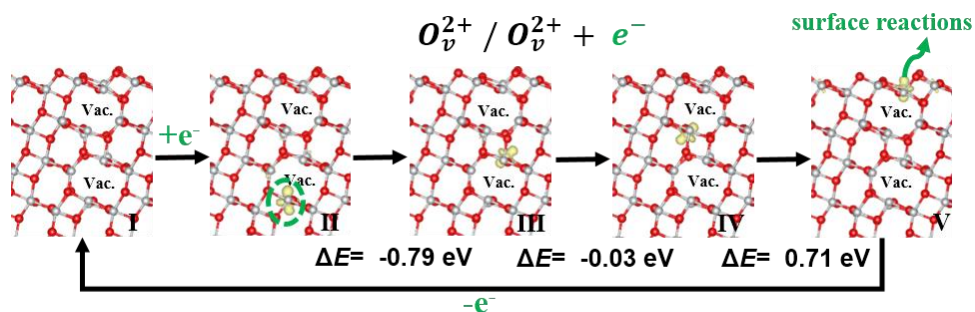


Figure S4. Calculated charge densities (iso-value of $0.008 |e|/\text{Bohr}^3$) and energies (ΔE) of an additional electron (indicated by green circles) migrating along two neighboring O_v^{2+} in an eight-Ti-layer $TiO_2(101)$ slab.

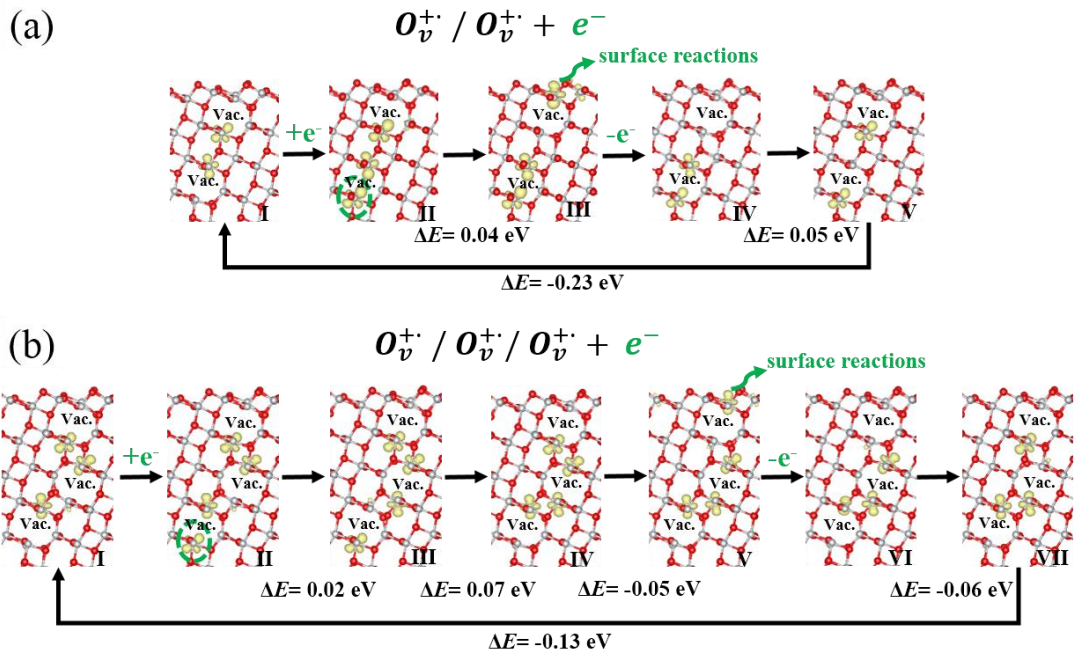


Figure S5. Calculated charge densities (iso-value of 0.008 $|e|/\text{Bohr}^3$) and energies (ΔE) of an additional electron (indicated by green circles) migrating along (a) a $O_v^{\cdot+}/O_v^{\cdot+}$ chain with different combination modes and (b) a longer chain of $O_v^{\cdot+}/O_v^{\cdot+}/O_v^{\cdot+}$ in eight-Ti-layer (101) slab.

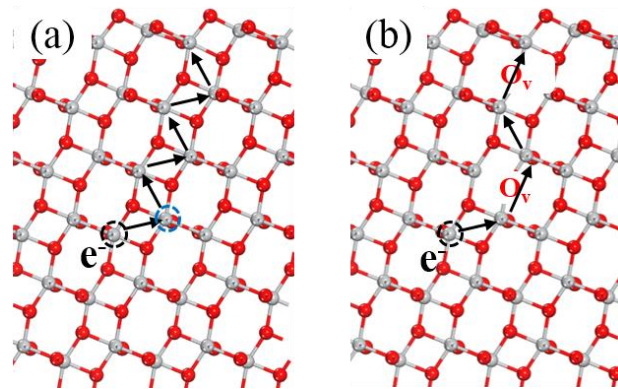


Figure S6. Schematic diagram of an excess electron, initially positioned at the fourth Ti-layer below the surface, migrating (a) in stoichiometric $\text{TiO}_2(101)$ or (b) along a O_v/O_v chain in defective slabs towards the surface, as indicated by black arrows.

2. Estimation approach on electron transfer efficiency

We developed an approach to roughly estimate the probability of a photoelectron successfully reaching the surface. Three major assumptions are made as follows:

(1) the electron-hole recombination probability is constant (defined as p), being irrelevant with the electron localization position (e.g., near the surface or in the bulk

region) or the presence/absence of O_v defects;

(2) for a photoelectron localized at one Ti cation, in the subsequent step it will either move to an adjacent Ti (probability: $1-p$) or recombine with a photohole;

(3) for each successful electron transfer step (apart from the recombination), considering the small migration barrier of less than 0.3 eV,¹ the chance of electron hopping (from this trapping site) to the nearest Ti cations obeys the Boltzmann distribution. Thus, the probability of a single-step electron transfer along a particular direction can be computed by dividing its odds by the sum of odds of all possible directions.

Regarding the comparison of photoelectron transfer efficiency in stoichiometric anatase $TiO_2(101)$ or along a vertical O_v^{++} chain, the minimum steps of surface-directed electron transfer (from the same starting point) is defined as n and m , respectively. As illustrated in Figure S6b, the presence of O_v introduces additional electron transfer channels (between two face-to-face Ti_{5c} at the O_v) with longer single-step migration distance pointing to the surface, and consequently the number of electron transfer steps (from the same initial position) along the vertical O_v^{++} chain would be less than that in stoichiometric slabs (i.e., $m < n$).

a. In stoichiometric anatase $TiO_2(101)$

In stoichiometric anatase $TiO_2(101)$ slabs, because of the obvious difference in electron transfer energies between the last surface-reaching step (from the subsurface) and the preceding $n-1$ steps, we analyzed separately the two parts:

I. Each Ti_{6c} cation (see black circle for example in Figure S6a) below the subsurface has four nearest Ti_{6c} neighbors with comparable electron trapping energies (± 0.01 eV), among which only one Ti_{6c} (dashed blue circle) positions closer to the surface that benefits the surface-directed photoelectron transfer. Thus, the probability of a single-step electron transfer toward the surface is $\frac{1-p}{4}$, while that for continuous $n-1$ steps of successful photoelectron transfer (before reaching the surface) would be $\left(\frac{1-p}{4}\right)^{n-1}$.

II. For the last surface-reaching step (from the subsurface), a subsurface Ti_{6c} cation also has four nearest Ti_{6c} neighbors. But the difference is that, while three of them all show comparable electron transfer energies (± 0.01 eV), electron transfer to the one on the surface is endothermic by 0.04 eV. Accordingly, based on the Boltzmann distribution $p_1/p_2 = \exp[\Delta E/(k_B \cdot T)]$ where p_1 and p_2 are the populations of the two possible electron trapping states/sites, the probability of photoelectron

arriving at the surface (with a 0.05 eV disadvantage in energetics) was estimated to be ~ 7 times lower than hopping to the other three migration sites, being $\frac{1}{22} \times (1 - p)$.

Therefore, the overall probability of n -step photoelectron transfer to the surface in stoichiometric anatase TiO₂(101) is $P_{stoichi} = 0.05 \times \frac{(1-p)^n}{4^{n-1}}$.

b. Along the vertical O_v⁺ chain

As depicted in Figure S6b, this pathway can also be broadly divided into two parts: I. a single-step electron collection by O_v⁺ and II. continues $m-1$ steps of electron migration along the vertical O_v⁺ chain.

For the part I, one electron is initially localized at a Ti_{6c} cation adjacent to a O_v⁺ (see black circle for example in Figure S6b), and it can either move to three neighboring Ti_{6c} with comparable electron transfer energies (± 0.01 eV), or to one Ti_{5c} at the O_v⁺ with exothermic energies of -0.25 eV. Similar to the surface-reaching step in stoichiometric anatase TiO₂(101), we can obtain the probability of the electron collection by O_v⁺ on the basis of Boltzmann distribution, which was deduced to be $\frac{23409}{23412} \times (1 - p)$.

For the part II, while electron transfer along the O_v⁺ chain is generally favored with a maximum energy cost of 0.03 eV, any deviations either to the odd Ti_{5c} of O_v or bulky Ti_{6c} nearby was found endothermic on average by 0.28 eV. Obviously, a single-step of electron migration along the O_v⁺ chain is at least 0.25 eV more favorable in energetics, which corresponds to 15897 times higher in probability than any deviations from the O_v⁺ chain according to the Boltzmann distribution. Thus, the probability of continuous $m-1$ steps of photoelectron transfer along the O_v⁺ chain would be $[\frac{15897}{15901} \times (1 - p)]^{m-1}$.

Overall, the probability of m -step photoelectron transfer to the surface along the vertical O_v⁺ chain is $P_{O_v^+} = \frac{23409}{23412} \times [\frac{15897}{15901}]^{m-1} \times (1 - P)^m$.

c. Comparison of the two pathways

From the analysis above, the probability for a photoelectron reaching the surface is largely determined by i) the migration distance below the surface (n or m), ii) the number of O_v involved, and iii) the step-by-step electron transfer energies. One can compare readily the probability of successful photoelectron transfer to the surface via the two pathways: $\frac{P_{O_v^+}}{P_{stoichi}} = 20 \times \left(\frac{15897}{15901}\right)^{m-1} \times 4^{n-1} \times (1 - P)^{m-n}$

$$> 20 \times \left(\frac{15897}{15901}\right)^{n-1} \times 4^{n-1}; n > m.$$

Reference

1. N. A. Deskins and M. Dupuis, *Phys. Rev. B*, 2007, **75**, 195212.