Supplementary Information for "Intrinsic Interaction between In-Plane Ferroelectric Polarization and Surface Adsorption"

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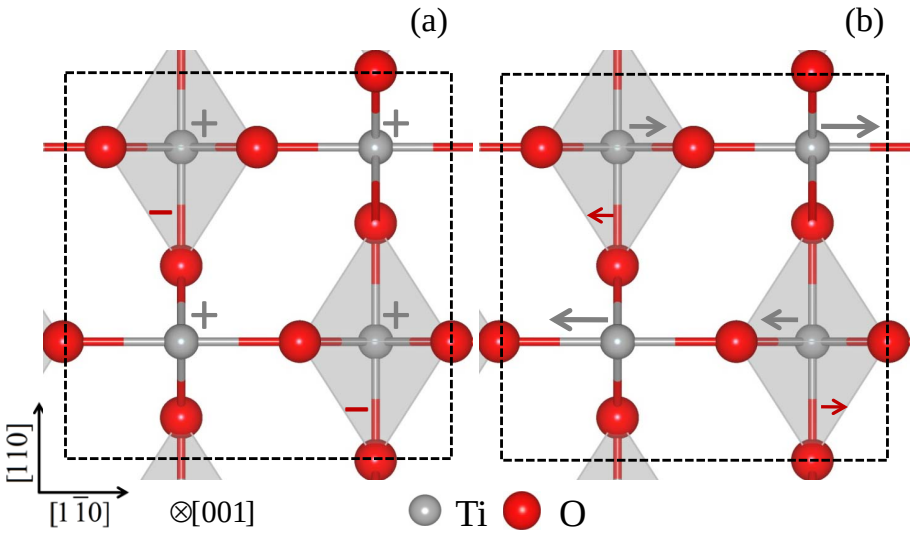

Figure S1: Schematic show of the spontaneous polarization of bulk rutile TiO_2 under tensile strain. The $(\sqrt{2} \times \sqrt{2} \times 1)$ supercells are marked by the dashed lines. The oxygen octahedrons can be divided into two groups, depending on whether the equatorial planes normal to $[1\bar{1}0]$ (OC_n) or in parallel to $[1\bar{1}0]$ (OC_p). Shaded areas mark the octahedrons of OC_p to guide the eyes. (a) When the strain is applied along [001] direction, both groups are equivalent to each other, and the six neighboring O atoms displace in the opposite directions of the Ti atom, as marked by red negative signs for O and grey positive signs for Ti, respectively. (b) When the strain is applied along $[1\bar{1}0]$ direction, OC_n and OC_p become inequivalent. As shown by the red arrows for O and grey arrows for Ti atoms, respectively, the six neighboring O atoms displace oppositely relative to the Ti atom in OC_p, while in OC_n the four O atoms in the equatorial planes displace in the same direction as the Ti atom while the two apical O atoms displace in the opposite direction.

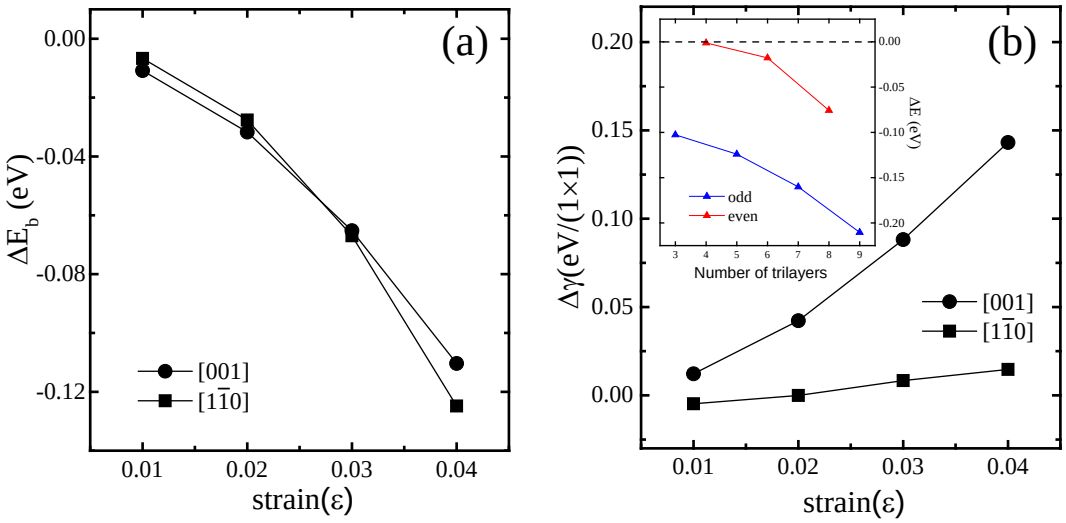

Figure S2: The changes of (a) the total energy of bulk TiO_2 and (b) the surface energy of the TiO_2(110) induced by the in-plane polarization. The bulk rutile TiO_2 is modeled by using a $\sqrt{2}\times\sqrt{2}\times1$ supercell. The TiO_2(110) surface is modeled as a (1×1) slab containing nine O-Ti-O trilayers and a vacuum with thickness of 15 Å. All the atoms are relaxed without constraints until the forces were converged to 0.01 eV/Å. The inset of (b) shows the polarization-induced change of the total energy of the slab as a function of the slab thickness (n) when $\varepsilon_{[001]} = 0.04$. It shows that the energy difference appears an odd-even oscillation behavior with n. Slabs with odd n are more favorable to polarization than even n.

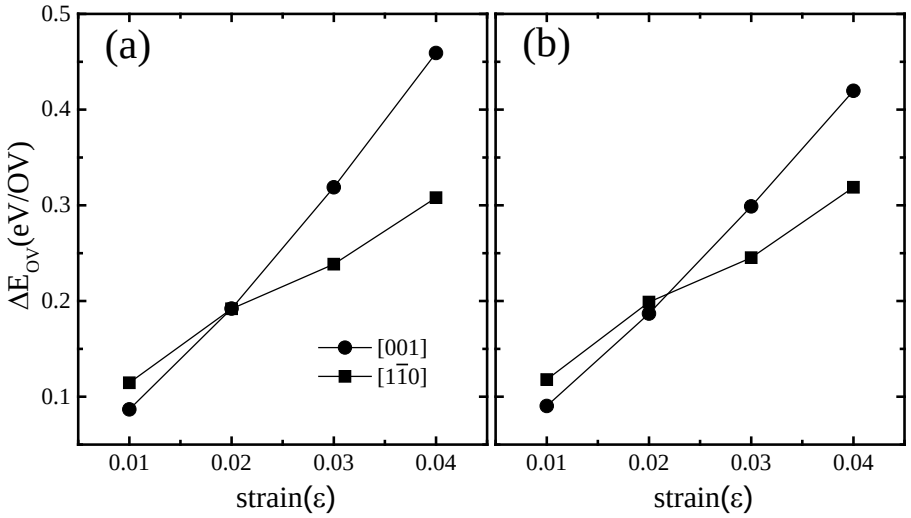

Figure S3: The changes of the formation energy of a bridging oxygen vacancy on TiO_2(110) induced by in-plane polarization. The surface is modeled as a slab of (1×4) supercell containing five O-Ti-O trilayers and a vacuum with thickness of 15 Å, (a) The atoms in the bottom trilayer are fixed as the same as in the corresponding bulk phase, and the other atoms were relaxed until the forces were converged to 0.01 eV/Å. (b) The surface with in-plane polarization is modeled as in (a), while the non-polarized surface is modeled by simply scaling the zero-strained non-polarized surface according to the specific strain.

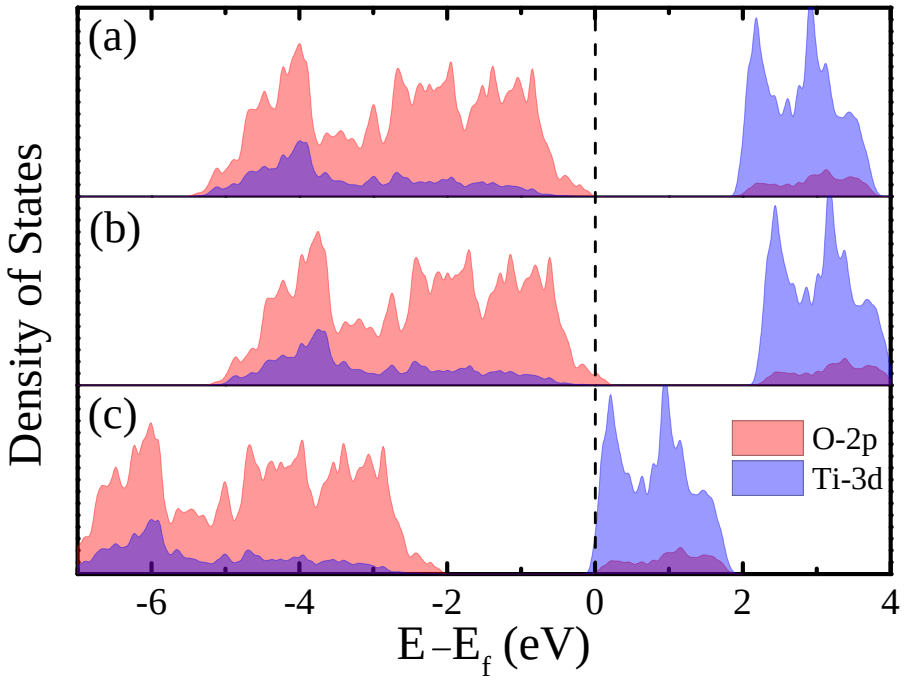

Figure S4: The partial density of states of bulk TiO_2 with doping concentration of (a) 0, (b) -0.075 and (c) 0.075 electron per unit cell when $\varepsilon_{[001]} = 0.03$. It suggests that the doping electrons occupy the Ti-3d orbitals while the doping holes are in the O-2p orbitals.