Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information For "Inherent Asymmetries in Ferroelectric/Semiconductor Composites due to Interface Chemistry: Analysis of the Oxygen Evolution Reaction in Ultra-Thin Titanium Dioxide/Barium Titanate Heterostructures"

1 Calculation of OER Profile

The OER takes place through a series of intermediate steps as shown in the main text of the paper. These intermediate steps fall in three main categories, as shown in Table 1. The first, a deprotonation step, involves an electron-hole pair, while the others (adsorption of water, and oxygen evolution, respectively) do not. Table 1 also shows the contributions to the Gibbs free energy change ΔG for each type of reaction. The scheme used here for calculating the Gibbs free energy change has been previously applied to anatase. The presence of an aqueous environment is ignored, which is a reasonable assumption when comparing the Gibbs free energies of structurally similar systems.

Table 1: **The three types of reaction steps in the OER.** 1 and 2 denote initial and final structures (substrate + adsorbate) for the reaction step. ΔE is the change in DFT energy from Step 1 to 2, ΔZPE is the change in zero-point energy, Δ(PV-TS)[x] is the enthalpy and entropy change of x at room temperature, where x is $\frac{1}{2}H_2$, O_2, or H_2O, and G[h^+ + e^-] is the Gibbs free energy of an electron-hole pair produced in TiO_2 with respect to the SHE. E[x] and ZPE[x] are the DFT energies and zero-point vibrational energies of the molecules that are added to or removed from the system.

Reaction Step	**Gibbs Free Energy Change (ΔG)**
$1+h^+ +e^- \rightarrow 2+H^+ +e^-$	$\Delta E_{1\rightarrow 2} + \Delta ZPE_{1\rightarrow 2} + E[\frac{1}{2}H_2] + ZPE[\frac{1}{2}H_2] + \Delta(PV-TS)[\frac{1}{2}H_2] - G[h^+ + e^-]$
$1 + H_2O \rightarrow 2$	$\Delta E_{1\rightarrow 2} + \Delta ZPE_{1\rightarrow 2} - E[H_2O] - ZPE[H_2O] - \Delta(PV-TS)[H_2O]$
$1 \rightarrow 2 + O_2$	$\Delta E_{1\rightarrow 2}+\Delta ZPE_{1\rightarrow 2}+E[O_2]+ZPE[O_2]+\Delta(PV-TS)[O_2]$

In Table 1, the ΔE contributions indicate changes to the internal energy, and the ΔZPE contributions indicate changes to zero-point vibrational energies. Both of these are obtained directly from DFT calculations. For internal energy changes ΔE, we relax the structural geometries for each intermediate step of the OER, on unsupported anatase (to obtain a reference profile) consisting of 8 MLs of TiO_2, and on positively and negatively polarized heterostructures. The zero-point energies were obtained by summing up the positive vibrational frequencies of the adsorbed species by performing a dynamical matrix calculation on the relaxed geometry. Table 2 shows the calculated zero point energies and DFT internal energies (E) for each step for positively- and negatively-polarized 4 ML heterostructures.

In our estimate of ΔG, we also include enthalpic and entropic contributions, but only for species that are introduced into or removed from the system – namely, the species $\frac{1}{2}H_2$, O_2 and H_2O. These contributions, at standard pressure and temperature, are taken from the CRC Handbook. The corresponding

Table 2: Zero point energies and DFT energies in eV for each OER step on positively- and negatively-polarized 4 TiO_2 ML heterostructures. Step 0 and Step 7 are identical and represent heterostructures with no adsorbates on the surface.

Reaction Step	**ZPE for $+P$ systems (eV)**	**ZPE for $-P$ systems (eV)**	**E$_{DFT}$ for $+P$ systems (eV)**	**E$_{DFT}$ for $-P$ systems (eV)**
0	0	0	-561.322	-561.446
1	1.264	1.281	-576.713	-576.563
2	0.633	0.464	-572.439	-570.318
3	0.147	0.164	-567.162	-566.632
4	1.449	1.535	-582.383	-581.541
5	0.909	0.908	-577.481	-575.929
6	0.279	0.214	-571.400	-570.444
7	0	0	-561.322	-561.446

term is indicated by (PV-TS)[x] in Table 1. The values of (PV-TS)[x] for aqueous H_2O, gaseous H_2, and gaseous O_2 are -0.57 eV, -0.31 eV, and -0.53 eV respectively. The corresponding value for $\frac{1}{2}H_2$ is simply one half the value for H_2, i.e. -0.155 eV. These values are taken from the CRC Handbook. Ignoring (PV-TS) contributions of the substrate amounts to neglecting enthalpic and entropic changes to the free energy of the solids during the OER, which are often small in comparison. We caution that this may not always be accurate, especially at higher temperatures. It is also worth nothing that ignoring the entropic contribution to ΔG for the substrate also means neglecting the configurational entropy of the substrate, which also may not be small if the adsorbed species possess many degrees of freedom for molecular rotation. Nevertheless, the rationale behind using these assumptions is that the entropic contributions are probably smaller in scale than the differences in adsorption energies that we are interested in.

The standard hydrogen electrode (SHE) is used as a reference for calculating the Gibbs free energy change for each reaction step, which amounts to setting the Gibbs free energy change for the reaction

$$H^+ + e^- \rightarrow \frac{1}{2}H_2$$

to zero. $G[h^+ + e^-]$ in Table 1 is set to $|e|U = 1.93$ eV, the energy required to generate an electron-hole pair in TiO_2 with respect to the SHE.