Titanium dioxide (TiO$_2$) is widely used in photocatalysis and solar energy conversion due to its many favorable properties, like stability against photocorrosion and proper band alignment relative to the water redox potentials [1–3]. However, the efficiency of TiO$_2$ is notoriously low, and efforts at improving it through modifications such as doping [4] or synthesis of (nano)crystals exposing highly reactive facets [5] have encountered only limited success. Among the possible alternatives to TiO$_2$, polar materials have recently attracted significant interest because their surface dipoles can react easily with charged species and supply built-in electric potentials to increase the carrier mobility [6,7]. However, control of the surface reactivity of these materials is difficult [8], e.g., because exposed surface dipoles often cause undesired atomic or electronic reconstructions and unexpected adsorption of charged species which can interfere with the reaction of interest [9–11]. Less well known than TiO$_2$ and polar semiconductors are heterostructures composed of stable TiO$_2$ thin films supported by a ferroelectric substrate [12,13]. Experimental studies have shown that the surface reactivity of TiO$_2$ is directly influenced and improved by the underlying ferroelectric domain structure, an effect that has been attributed to the combined efficient absorption and charge separation in the ferroelectric substrate and transport across the TiO$_2$/substrate interface [12,13]. Despite some encouraging results [13,14], however, the interest in such TiO$_2$/ferroelectric heterostructures has remained limited. In particular, their physical properties are largely unexplored and an atomic-scale understanding of their reactivity is missing.

We present here a first-principles density functional theory (DFT) study of TiO$_2$/ferroelectric heterostructures, which provides evidence that these composite materials can have a substantially enhanced reactivity relative to TiO$_2$. We focus on model heterostructures composed of a TiO$_2$ (001) film of anatase (the TiO$_2$ polymorph most efficient for photocatalysis [15]) supported by a nearly ferroelectric SrTiO$_3$ (STO) substrate that can easily acquire a macroscopic polarization in the presence of an external perturbation such as electric field and epitaxial strain [16,17]. These structures are denoted TiO$_2$/STO in the following. Anatase has a small lattice mismatch with STO, so it can be grown on STO epitaxially [18]. While defects, e.g., oxygen vacancies, are almost invariably present in the experimentally prepared materials, it is reasonable to restrict to ideal, defect-free heterostructures in this first study. We probe the surface reactivity by investigating the oxygen evolution reaction (OER), which is known to be the bottleneck of water splitting [19,20], and show that the activity is directly related to the changes of the dynamically induced polarization in the supported TiO$_2$ film during the reaction. By varying the strain and thickness of the STO substrate, we further show that the strain and the induced dipole can be synergistically tuned to optimize the surface reactivity for the reaction of interest.

Our study is based on spin-polarized DFT calculations in the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [21] and the plane-wave-pseudopotential scheme as implemented in the PWSCF code of the QUANTUM ESPRESSO package [22]. Selected calculations using the DFT + $U$ approach [23] are discussed below. We consider TiO$_2$/STO model heterostructures composed of four anatase TiO$_2$(001) layers on top of seven (four TiO$_2$ and three SrO) layers of STO, with the two bottom layers (corresponding to one unit cell) fixed at the atomic positions of strained polar bulk STO (Fig. 1). As usual, below STO three Pt(001) layers are included to screen the dipole moments of STO [24,25]. We use a $(2 \times 1)$ surface cell, with a $2 \times 4 \times 1$ mesh to sample $k$ space. Consecutive slabs are separated by a $\sim 10$ Å vacuum with a dipole correction layer. All structures are relaxed until residual forces are smaller than $7.35 \times 10^{-4}$ au. With this setup, the computed in-plane lattice constants of TiO$_2$...
anatase and STO are 3.786 and 3.938 Å (+4.0% relative to anatase) and corresponding experimental values are 3.782 and 3.905 Å (+3.3%). The induced polarization in TiO$_2$ is determined from the average cation-anion displacements ($\Delta z = z_{Ti} - z_{O}$) multiplied by the relevant effective charges (details in Supplemental Material [26]). We approximate the charges of TiO$_2$/STO [27] by the effective charges of strained bulk TiO$_2$ that we calculate using the Berry-phase method.[28]

In Fig. 1, the effects of the STO polarization on the band edges and work function of TiO$_2$ are illustrated for two heterostructures, (TiO$_2$/STO)$_\pm$, with opposite polarizations of the bottom STO layers of $\pm 0.8$ C/m$^2$, which result from a STO compressive strain of 4%. The electrostatic potential energy profiles, Fig. 1(B), and densities of states (DOS), Fig. 1(C), show that there is a substantial difference, ~2.5 eV, between the work-functions of the two TiO$_2$ surfaces and a nearly rigid shift of similar magnitude between the DOS curves of the two heterostructures. Analysis of the layer resolved DOS (Fig. S2-1 in the Supplemental Material [26]) further shows that the shift is similar for the different TiO$_2$ layers up to the top surface. This may be due to the relatively low static dielectric constant of anatase along the [001] direction ($\varepsilon_{\parallel} = 22.7$ [29]).

OER free energy profiles on TiO$_2$/STO are calculated following a simple, yet effective scheme [30] that has been recently applied to various unsupported TiO$_2$ rutile [19,30] and anatase [20] surfaces. The water environment is not included [19,30], an acceptable approximation for studying trends in structurally similar systems [31]. The $1 \times 4$ reconstruction of anatase (001) is destabilized under electrochemical conditions and is also neglected [20]. The Gibbs free energy changes ($\Delta G$) for the four OER steps are determined by combining DFT total energy and vibrational frequency calculations at $T = 0$ K with standard thermodynamic data for molecules in the gas and liquid phases. We further use the standard hydrogen electrode (SHE) as the reference potential [30], with the dependencies on $p$H and $U$ included as simple additional terms in $\Delta G$ [30]. Following Ref. [20], we take $p$H = 0 and $U = 1.93$ V, which corresponds to an overpotential of 0.7 V, as found experimentally for rutile TiO$_2$ nanowires [32].

In Fig. 2 we compare our computed OER free-energy profiles for the heterostructures of Fig. 1(A) and on unsupported anatase (001), for which our results agree well with previous DFT studies [19,20]. For unsupported anatase (black dotted line) there is a thermodynamic barrier of 0.45 eV, which originates from the first deprotonation of the first adsorbed water molecule (step 1 $\rightarrow$ 1'). For negatively polarized (TiO$_2$/STO)$_-$, the free-energy profile (blue line) is almost identical to that of unsupported TiO$_2$, despite the large negative polarization ($-0.8$ C/m$^2$) of the STO substrate. By contrast, for positively polarized (TiO$_2$/STO)$_+$, there are major differences (red line), especially for the 1 $\rightarrow$ 1' step, whose $\Delta G$ changes from endothermic to strongly exothermic. As a result, the overall thermodynamic barrier is strongly reduced, from 0.45 eV on unsupported TiO$_2$ to $\sim 0.09$ eV on (TiO$_2$/STO)$_+$. To test the robustness of this prediction, we determined $\Delta G$ for the key 1 $\rightarrow$ 1' step using the DFT(GGA) $+ U$ approach, that is widely applied to transition metal oxides [33–35], including studies of the OER [36]. Using $U = 3$ eV for the Ti 3d states, a value that works well for both TiO$_2$ [33,34] and STO [35], we found no significant difference from the results in Fig. 2 (see Fig. S1 of the Supplemental Material [26]). We also examined the effect of the TiO$_2$ slab thickness and found that the 1 $\rightarrow$ 1' step remains exothermic ($\Delta G = -0.6$ eV at the GGA level) when the thickness of the TiO$_2$ film is increased from four to eight layers.
Material[26]). In experiments, this dynamically induced field oxygen adatom O− increases to ∼1 eV inside the TiO2 layers, as well as a large electric field of ∼0.1 eV/Å (see Figs. S2–2–S2-6 in the Supplemental Material [26]). In experiments, this dynamically induced field could help separating electrons and holes and boost the diffusion of the holes toward the TiO2 surface during the intermediate steps of the reaction. Typical switching times of polar domain wall (∼nanometers) in oxide films vary from nanosecond to subpicosecond [37,38]. The switching time of the relevant dipoles (∼Å) at the TiO2 surface is expected to be much faster, so they can respond promptly to the changes in the charge of the absorbed species during the reaction, whose characteristic times have a lower limit of ∼1.5 ps [39].

Using strain to control the surface reactivity is an appealing possibility [40–42]. To examine the effect of strain on the reactivity of TiO2/STO, we studied the OER on various strained (TiO2/STO)− heterostructures, with the STO polarization proportional to the strain [16]. Our results are reported in Fig. 4, where the strain is referred to anatase, so that a tensile strain of +3.8% is close to the computed equilibrium lattice parameter of STO. Configuration 2 (after adsorption of the second water molecule) is the most affected by epitaxial strain, with a free energy drop of almost 2 eV when the strain changes from +3.8% to −1%. This effect can be understood as follows. Under zero or compressive strain, the large positive STO polarization leads to large surface

![Image](https://example.com/image.png)
and can thus bind to the twofold oxygen on the TiO surface (see Ref. [20] and Fig. S2-4 [26]). To sum up, the reactions presented so far, the atomic positions of the bottom STO layer were fixed to those of strained bulk STO so as to mimic a thick ferroelectric STO layer (Fig. S3 in the Supplemental Material [26]). However, it is experimentally challenging to prepare thick coherent films with large epitaxial strains of 3%–4% [17], as used to obtain the profiles shown in Figs. 2 and 4. As an alternative possibility, we have considered thin STO films without any built-in polarization, epitaxially compressed to match the TiO2 lattice. Figure 5 shows the OER profiles for TiO2/STO heterostructures in which all atomic positions in the STO film are fully relaxed. For comparison, also shown are two OER profiles already reported in Fig. 2, for pure TiO2 (black dotted line) and the positively polarized TiO2/STO heterostructure (red line) with a thick STO substrate. The heterostructure in the inset shows the STO layers which are either fully relaxed (r) or kept fixed (u) to represent a thin film or thick substrate, respectively.

In conclusion, our study shows that the OER activity of heterostructures of TiO2 on a polar substrate can be strongly enhanced relative to unsupported TiO2 due to dynamical dipoles induced in response to the charge on the adsorbed species. By utilizing substrate polarization and strain as control parameters, these versatile structures hold...
significant promise as new efficient catalysts for water splitting and other (photo)chemical reactions.

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