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Modeling Electron Storage at the Interface between Au and anatase-TiO₂ under Ambient Conditions

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ABSTRACT

Au supported on TiO₂ is a promising photocatalyst due to its ability to catalyze reactions under illumination and store electrons for sustained reactivity in the dark. Using Density Functional Theory (DFT), we investigate the structural evolution and reactivity of the Au/anatase-TiO₂(001) interface under realistic conditions. Phase diagrams and charge analysis reveal that the Au/TiO₂ interface can reversibly store electrons by transitioning between different charge states and structures via oxidation and reduction. This electron storage and the associated reducing potential, along with the atomic arrangement, promotes key photoelectrochemical reactions, such as oxygen reduction reaction (ORR) and CO₂ reduction reaction (CO₂RR). Lattice titanium and oxygen vacancies act as active sites, with the 2e-ORR pathway (H₂O₂ formation) kinetically favored due to a lower proton-coupled electron transfer barrier. The interface also facilitates CO₂ activation, which is challenging on bare Au. These findings provide a foundation for optimizing Au/TiO₂ composites for energy storage and conversion.

KEY WORDS

Au, TiO₂, electron storage, oxygen reduction reaction, CO₂ reduction reaction

INTRODUCTION

The rise in CO₂ emissions from fossil fuel combustion is a leading driver of climate change, prompting urgent efforts to transition to renewable energy sources and develop methods for CO₂ capture and conversion^{1,2}. Solar energy is particularly attractive as a renewable alternative, but its intermittent availability presents challenges. One promising solution is to integrate solar energy harvesting with CO₂ reduction technologies, enabling both energy conversion and storage in a single system³.

TiO₂ has long been a popular semiconductor for photocatalytic applications due to its stability and low cost⁴. However, traditional TiO₂ suffers from fast electron-hole recombination and a large band gap that limits its absorption to the UV region. These drawbacks necessitate modifications to enhance its performance in photocatalysis. Researchers have explored several strategies to

overcome these limitations, including the use of TiO₂ with specific morphologies (e.g. nanoparticle shape, size, and faceting⁵) and hierarchical structuration (e.g. inverse opals⁶), polymorph (e.g. rutile *vs* anatase, especially the more reactive a-TiO₂(001) facet⁷), or coupling TiO₂ with co-catalysts⁸ such as metals⁹ or metal oxides¹⁰. These modifications are designed to improve charge separation, extend absorption to the visible light spectrum, and introduce new active sites for catalytic reactions. Among the various co-catalysts, Au nanoparticles have garnered attention due to several key advantages. First, Au enhances charge separation at the Au/TiO₂ interface, mitigating the fast electron-hole recombination typical of TiO₂. Second, Au provides active sites for catalytic reactions, which are crucial for ORR and CO₂RR. Third, Au nanoparticles exhibit localized surface plasmon resonance (LSPR) effects, which enhance photon absorption in the visible spectrum¹¹. Finally, an unexpected and significant advantage of Au/TiO₂ is its ability to store electrons, enabling the Au/TiO₂ interface to maintain catalytic activity even after illumination is removed. This electron storage effect was initially discovered in WO₃/TiO₂¹² but was later found in many TiO₂ composites¹³. This capability extends the operational window of the catalyst, making it highly attractive for sustained catalytic applications.

Building on previous research demonstrating the extended post-illumination reactivity of Au/TiO₂ systems⁹, which showed that Au nanoparticles on a-TiO₂(001) have superior charge storage ability compared to a-TiO₂(100) and a-TiO₂(101), this study aims to deepen our understanding of the charge storage and catalytic mechanisms at the Au/a-TiO₂(001) interface. By employing DFT calculations, we investigate the thermodynamics and kinetics of ORR and CO₂RR at this interface, with a particular focus on its behavior under various environmental conditions. Our findings reveal new insights into how Au/TiO₂ can be optimized for energy storage and conversion applications, offering a promising pathway for integrating renewable energy technologies with CO₂ utilization.

METHODS

DFT calculations were performed using the Vienna ab initio simulation package (VASP)¹⁴. The exchange-correlation energy was calculated using the Perdew-Burke-Ernzerhof (PBE) functional¹⁵. The projector-augmented wave (PAW) method¹⁶ was used to describe the core electrons. The one-electron wave functions were developed on a basis set of plane waves with an energy cutoff of 400 eV. The density-dependent energy correction (dDSC) method¹⁷ was used to account for van der Waals forces. Energy differences between steps in the self-consistent field (SCF) cycles were converged to 10⁻⁶ eV. Atomic positions were relaxed until the forces were less than 0.05 eV/Å. To correct for the self-interaction error of Ti 3d electrons, a Hubbard-like repulsion term was added using Dudarev's approach (PBE+U)¹⁸, with U_{Ti} = U - J = 3.5 eV, determined using linear response¹⁹. To model solvation, we used an implicit solvation model²⁰ describing the solvent as a dielectric medium where the charge species in the electrolyte are modeled by a continuous charge density determined by the linearized Poisson-Boltzmann approach for all calculations. For kinetic studies involving proton transfer, a hybrid solvation scheme was adopted, combining implicit model with four water molecules to capture local hydrogen bonding.

Electrochemical potential was treated using a hierarchical approach. The computational hydrogen electrode (CHE) method²¹ was used for most thermodynamic studies. For potential-dependent processes such as charge storage, CO₂ adsorption, and reaction barriers, we applied the surface charging (SC) method²²⁻²⁶.

To represent the Au/TiO₂ interface observed experimentally, where Au nanoparticles are dispersed

on TiO_2 ⁹, we employed a periodic Au rod model^{27,28} that captures the local interfacial structure while avoiding the computational cost of a full Au nanoparticle. The $\text{TiO}_2(001)$ substrate was chosen based on prior experimental findings⁹ demonstrating its superior electron storage capacity compared to other TiO_2 surfaces. The model is shown in Figure 1. The substrate was modeled as a $p(4\times 4)$ 3-layer $\alpha\text{-TiO}_2(001)$ slab with lattice constants $a = 3.82 \text{ \AA}$, $c = 9.52 \text{ \AA}$, while the fcc Au rod ($a = 4.15 \text{ \AA}$) was adhered along the $\text{TiO}_2[010]$ direction to minimize lattice mismatch. The Au rod and the top TiO_2 layer were relaxed. The Brillouin zone was sampled at the Γ point (see Supplemental Methods Section 5 for details).

RESULTS AND DISCUSSION

Au/ TiO_2 stability diagram in experimental conditions

The structure of Au/ TiO_2 shown in Figure 1 is a simple stoichiometric model that does not account for environmental influences. Indeed, the surface structure of the Au/ TiO_2 interface can vary significantly depending on experimental conditions. For instance, during thermocatalytic CO oxidation reactions, the Au/ TiO_2 is in equilibrium with gas-phase CO, O_2 (and H_2O) at certain partial pressures and elevated temperatures^{29,30}. In photo/electrocatalytic conditions, the Au/ TiO_2 is in aqueous solution at room temperature and pressure, where pH and potential are variable factors. To determine the interface structure of Au/ TiO_2 under realistic experimental conditions, we compared the interface stability of various species, such as the formation of $\ast\text{O}$, $\ast\text{O}_2$, $\ast\text{H}$, $\ast\text{OH}$, $\ast\text{H}_2\text{O}$ (stars indicate adsorbed species) and O_v (oxygen vacancies) (see Supplemental Methods Section 1 for details). We also considered the coverage effect of each species. For species likely to co-exist under experimental conditions, such as $\ast\text{H}$ and O_v , we thoroughly studied their synergistic coverage effects.

The results are presented as two phase diagrams, which serve as references for gas-phase thermocatalysis, showing the Au/ TiO_2 interface in equilibrium with O_2/H_2 (Figure 2a) or $\text{H}_2\text{O}/\text{H}_2$ (Figure 2b). When in equilibrium with O_2/H_2 , H adsorption occurs under H-rich conditions, favoring $\text{TiO}_2(001)$ and not Au. Such $\ast\text{H}$ spillover from Au to TiO_2 has been observed in recent experiments³¹. Also, TiO_2 surface hydroxylation (reduction) weakens the Au- TiO_2 binding and increases the Au/ TiO_2 contact angle, according to Young-Dupré's law³². $\text{OH}/\text{H}_2\text{O}$ adsorption occurs under O-rich conditions, disrupting the Ti-O bond on the TiO_2 surface and stabilizing it by releasing surface tension. O_v formation occurs under O-poor, H-poor conditions. The surface may also adopt a pristine configuration where none of the tested adsorbates are thermodynamically favored under O-moderate, H-poor conditions. When in equilibrium with $\text{H}_2\text{O}/\text{H}_2$, H adsorption occurs under H-rich, H_2O -rich conditions, while OH adsorption occurs under H_2O -rich, H-poor conditions. O_v formation occurs under H_2O -poor, H-rich conditions.

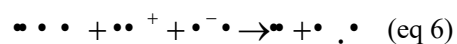
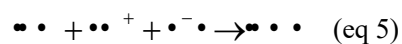
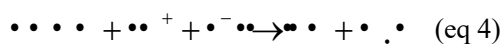
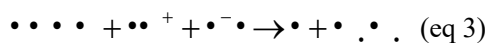
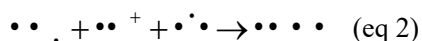
By applying the computational hydrogen electrode (CHE) method²¹ to account for the influence of the potential (see Supplemental Methods Section 2 for details), we also present the results as a Pourbaix diagram, applicable to aqueous-phase electrocatalysis, showing the Au/ TiO_2 interface under certain electrode potentials and pH levels (Figure 3a). At positive potentials, the interface between Au and TiO_2 is populated with $\ast\text{OH}$ adsorbates; at neutral potentials, with $\ast\text{H}$ adsorbates; and at negative potentials, it mainly shows O vacancies. To better understand the reversible electron storage mechanism of Au/ TiO_2 , we performed surface charging²² and Bader charge analysis³³. When Au/ TiO_2 is uncharged, the Fermi level (E_F) is in equilibrium with Au ($U = +0.7 \text{ V}$ vs SHE), and the TiO_2 surface is hydroxylated with $\ast\text{OH}$. At this state, the physical charge introduced by surface

charging is $-2.5 e^-$, distributed as $-1.33 e^-$ on Au and $-1.17 e^-$ on TiO_2 , since electrons are withdrawn from the electrode at positive potential. When Au/ TiO_2 is fully charged, E_F aligns with the conduction band of TiO_2 ($U = -0.7$ V), and the TiO_2 surface is reduced with O_v . At this state, the physical charge is $-0.75 e^-$, with $+5.08 e^-$ on Au and $-5.83 e^-$ on TiO_2 , resulting in a net total physical storage of $1.75 e^-$. Transitions between these $*OH$, $*H$, and O_v states occur through protonation and water desorption processes. The shift from $*OH$ to $*H$ involves the protonation of $*OH$ to $*$ and H_2O , followed by the formation of $*H$. The transition from $*H$ to O_v involves further protonation and water desorption, where $*O_{lattice}H$ reacts with proton to produce H_2O and O_v . Each O_v corresponds to two chemically stored electrons, while each $*OH$ corresponds to one chemical electron deficit, resulting in a total chemical storage of $9 e^-$. Together, considering both physical and chemical contributions, $10.75 e^-$ are stored during the entire charging process, with $6.41 e^-$ on Au and the rest on TiO_2 . During the photo-charging process, the electrons are not only physically stored in the double-layer capacitor formed at the Au-solvent interface, but also chemically as oxygen vacancies. Releasing the chemically stored electrons is a slower process, which is key to enabling a prolonged storage time, as observed minutes after illumination is removed.

Oxygen reduction reaction from stored electrons at Au/ TiO_2

The interaction between O_2 and the charged Au/ TiO_2 interface, where photoelectrons are stored, has the potential to produce reactive oxygen species, such as hydrogen peroxide. The competing, undesirable reaction is to produce unreactive water from total reduction instead. The reaction is analogous to the oxygen reduction reaction seen in fuel cells with a major difference: here, for delayed photocatalysis, the two-electron reaction forming hydrogen peroxide is favored, while in fuel cells the four-electron reduction forming water is targeted, since it produces more electrical energy.

The first step is O_2 adsorption (eq 1). Depending on the catalyst and conditions, both 2e-ORR and 4e-ORR are possible. The 2e-ORR involves two reduction steps and produces H_2O_2 (eq 2, 3), while the 4e-ORR involves four steps and produces H_2O (eq 2, 4-6)³⁴.



In the framework of the CHE method, the energy of ($H^+ + e^-$) pairs is considered as the energy of $1/2 H_2$ at a potential of 0V vs SHE. While in the framework of SC method, the energies of each intermediate are calculated at a specific potential. We start with a thermodynamic analysis using CHE. As an example, the free energy change of the first electron transfer step (ΔG_1 for eq 2) was calculated as:

$$\Delta G_i = G_{*OOH} - G_{*O} - \frac{1}{2} G_{H_2} - eU - k_B T \ln(10) \cdot pH \quad (\text{eq 7})$$

where G represents the DFT-calculated free energies, e is the elementary charge (1.602×10^{-19} C), U is the applied potential, k_B is Boltzmann constant, T is temperature (298 K), and pH is the pH level in the solution. Other steps are calculated similarly (see Supplemental Methods Section 3 for details). The least negative U at which all steps are downhill in free energy is defined as the limiting potential U_L .

We thoroughly investigated the reactions and active sites at 0 V (partially charged) and -0.7V (fully charged) during the charging-discharging process in the post-illumination ORR.

At 0 V, the Au/TiO₂ interface is populated with *H adsorbates (4H-phase). Figure 4a shows the energy profile at this potential. We investigated the following active sites: **(I) Au sites:** these sites are +1.20 eV endothermic for the O₂ adsorption step. **(II) Ti sites in the TiO₂ lattice:** these sites are exothermic for all steps. The limiting potential is +0.03 V for 4e-ORR from the *OH→H₂O step, and +0.18 V for 2e-ORR from the *OOH→H₂O₂ step. **(III) Ti_{int} sites at the interface:** these sites are +0.2 eV endothermic for O₂ adsorption, but exothermic for all other steps. The limiting potential is +0.04 V for both 4e-ORR and 2e-ORR from the *O₂→*OOH step. One can note that limiting potentials are weakly positive, which means that the overpotentials are high (about 1 V, since the thermodynamic equilibrium potential is +1.23 V vs SHE). This indicates that Au/TiO₂ is not an efficient ORR electrocatalyst. This is not a problem here since photo-induced charging places the system at a low potential, where the reaction occurs.

At -0.7 V, the Au/TiO₂ interface is populated with oxygen vacancies (4O_v-phase). Figure 4b shows the energy profile at this potential. We investigated the following active sites: **(I) Au sites:** similarly, these sites are +1.03 eV endothermic for O₂ adsorption. **(II) O_v sites in the TiO₂ lattice:** the limiting potential is -0.48 V for 4e-ORR from the *OH→H₂O step, and -0.24 V for 2e-ORR from the *O₂→*OOH step. **(III) Ti sites in the TiO₂ lattice:** these sites are +0.19 eV endothermic for O₂ adsorption, but exothermic in all other steps. The limiting potential is > -0.3 V, indicating the reaction can occur whenever the Au/TiO₂ interface is in the O_v-phase. **(IV) O_{v,int} sites at the interface:** these sites strongly prefer dissociative 4e-ORR, where *OOH dissociates into *H+*OH rather than forming H₂O₂. The limiting potential is -0.86 V for 4e-ORR from the *O→*OH step.

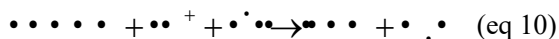
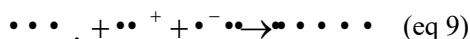
The overall thermodynamic picture is shown in the rainbow bar in Figure 4d. When fully charged, the Au/TiO₂ is in O_v-phases, with both lattice Ti and O_v sites catalyzing ORR (effective potential -0.7 V). As the stored electrons are consumed and the potential becomes less negative, the Au/TiO₂ transitions into H/O_v hybrid phases, then H-phases. During this transition, oxygen vacancies disappear, the Au/TiO₂ interface contact angle changes, and newly exposed Ti_{int} sites start catalyzing ORR.

We now discuss the role of kinetics in understanding the selectivity between reactive H₂O₂ formation (2e-ORR) or water formation (4e-ORR). As part of this analysis, we investigate the proton transfer process by utilizing a solvated H⁺(H₂O)₄ water cluster to study its interaction with *OOH (Figure 5). The nudged elastic band (NEB) method is used to find the transition state (TS) along the reaction pathway between initial state (IS) and final state (FS). Then, the surface charging method was applied on IS and TS to find the potential dependence of the activation barrier. At a fully charged state of -0.7 V, the active sites on Ti favor the reduction of *OOH into *O+H₂O over the formation of H₂O₂, with reaction energies of -2.23 eV and -0.24 eV, respectively. However, the activation

barrier for forming H₂O₂ is lower (0.10 eV) compared to that for H₂O (0.30 eV). A similar trend occurs at the partially charged state with a potential of 0 V, where the reduction to H₂O is more thermodynamically favorable, yet its activation barrier remains higher. This kinetic behavior explains why H₂O₂ is detected in dark experiments rather than just H₂O⁹, as the lower activation barrier for H₂O₂ formation plays a significant role when thermodynamic advantages are less pronounced^{34,35}.

Au/TiO₂ in photocatalytic CO₂ reduction reactions

The CO₂ electroreduction reaction (CO₂RR) is an important electrochemical reaction that enables the conversion of CO₂ into valuable products, such as CO, CH₄, C₂H₄, and CH₃CH₂OH. CO, the simplest product of CO₂RR, involves two electron transfer steps (eq 8, 9)³ (see Supplemental Methods Section 4 for relative energy calculation details). Ag and Au have been demonstrated as the most effective metal catalysts for converting CO₂ to CO, with CO₂ adsorption being the rate-determining step. On Au surfaces, the successive reductions of *CO₂ proceed more easily than its initial adsorption, as demonstrated in previous studies and in our calculations (Figure 6a, olive line). A significant challenge for metal catalysts lies in their limited ability to adsorb CO₂. The unique electronic and geometric structures at the Au/TiO₂ interface may provide potential sites for enhanced CO₂ activation.



We focus on the energy profile of CO₂RR at -0.52V vs SHE, which is the formal equilibrium reduction potential for the conversion of CO₂ to CO. Based on the Pourbaix diagram (Figure 3), the Au/TiO₂ interface is populated with oxygen vacancies (4O_v-phase). We investigated the following active sites: **(I) Ti site**, which exhibits a +1.07 eV endergonic adsorption energy for CO₂. **(II) O site**, where both CO₂ adsorption and *CO₂ reduction are endergonic, by +0.16 eV and +1.18 eV, respectively. **(III) Au/Ti site**, where the *CO₂ reduction is the potential-determining step (endergonic by +0.57 eV), and the other elementary steps are all exergonic. After *CO formation, it can either desorb (endergonic by +0.31 eV) or be hydrogenated into *CHO (endergonic by +0.06 eV), enabling further reduction toward CH₄. **(IV) Au/O_v site**, where the *CO₂ reduction is also potential determining (endergonic by +0.28 eV), and other steps are exergonic. Formed *CO can either desorb (endergonic by +0.03 eV) or be hydrogenated into *CHO (exergonic by -0.10 eV). CO₂ generally exhibits weak binding on Au(111), rutile-TiO₂(110), and a-TiO₂(101) facets due to its inert nature. However, the Lewis basicity of a-TiO₂(001)³⁶ and the electron reservoir function of Au work synergistically to facilitate the exergonic binding of CO₂ at the interface (Au/Ti and Au/O_v sites). The binding of CO₂ is characterized by its bent configuration, which pulls an Au atom slightly out of the plane of the Au rod. The C atom of the CO₂ binds to the Au atom, and one O atom binds to surface Ti atom (Figure 6a, structure table, row 1, column 3 and 4). The net Bader charge on *CO₂ is 0.8 to 0.9 e⁻, confirming its CO₂⁻ nature with the electron transfer from Au. The potential dependence of CO₂ adsorption energy is further explored using surface charging, with results showing exergonic CO₂ adsorption at both sites at -0.52 V or more negative potentials (Figure 6b).

It should be noted that exergonic CO₂ adsorption is not seen on Au electrocatalyst, where in contrast CO₂ adsorption appears as the most difficult step along the electroreduction pathway³.

For the subsequent *CO₂ to *COOH step, we investigate the proton transfer process using a solvated H⁺(H₂O)₄ cluster model, similar to that employed in our ORR studies. NEB is being used to find the TS. Then, surface charging method is being used on TS and FS. The barrier is calculated as (G_{TS}-G_{FS})^{SC}+(G_{FS}-G_{IS})^{CHE}. For CO₂ protonation at the Au/Ti site and Au/O_v site, the barriers are 0.40 eV and 0.81 eV, respectively (Figure 6c; see Figure S3 for detailed discussion). While the use of H⁺(H₂O)₄ model tends to underestimate the reaction barrier for the PCET step³⁸, applying more negative potentials and more basic conditions¹ further reduces this barrier, enabling the reaction to occur at a reasonable rate at room temperature.

Therefore, due to its ability to bind CO₂ and perform reduction with moderate barrier at the equilibrium potential, Au/TiO₂(001) should present low overpotential for CO₂RR and therefore high performance for that reaction. Multiple experiments have confirmed that Au/TiO₂-based systems exhibit enhanced CO₂ reduction activity³⁹⁻⁴³. More specifically, one study found that reduced Au/TiO₂ interface with O_v increases reactivity and further provides potential pathways for C-C coupling³⁹. This experimental observation is consistent with our prediction that O_v at the Au/TiO₂ interface plays an important role and indicates a possible direction for further investigation.

CONCLUSION

In this study, we employed DFT calculations to investigate the interface between an Au nanoparticle and an a-TiO₂(001) surface and its potential for catalytic and energy storage applications. Our findings highlight the versatility of this material, especially under ambient conditions relevant to ORR and CO₂RR.

We demonstrated that the Au/a-TiO₂(001) interface exhibits stable phase behavior under a relevant range of chemical potentials, as shown in the phase diagrams (Figures 2). The interface's ability to adapt to both O₂/H₂ and H₂O/H₂ equilibrium conditions enables effective catalytic activity for various reactions. The Pourbaix diagram (Figure 3) further reveals that Au/TiO₂ can reversibly store electrons, transitioning between different charge states, which supports sustained catalytic performance even after the removal of illumination.

For the formation of active oxygen species, we identified that both lattice Ti and O_v sites thermodynamically favor the (unwanted) 4e-ORR pathway producing unreactive H₂O at both the fully charged state (-0.7 V) and the partially charged state (0 V). However, from a kinetic perspective, the desired 2e-ORR pathway producing reactive hydrogen peroxide H₂O₂ is easier due to its lower activation barrier, which explains the selective formation of H₂O₂, particularly in the absence of illumination. This distinction between thermodynamic and kinetic accessibility helps clarify the experimentally observed production of H₂O₂ despite the thermodynamic preference for the complete reduction to H₂O.

For CO₂RR, we found that the Au/TiO₂ interface facilitates CO₂ adsorption and reduction, particularly at Au/Ti and Au/O_v sites, where electron storage in Au and the Lewis basicity of a-TiO₂(001) enhance CO₂ binding. The synergy between Au and TiO₂ enhances the catalytic activity, making this material a promising candidate for CO₂ conversion.

In summary, our computational study establishes Au-TiO₂ as a highly adaptable material with dual functionality—serving as an energy storage medium, as well as a post-illumination catalyst for the formation of reactive oxygen species and for CO₂RR. These findings underscore its promise for

sustainable energy applications, offering a pathway for continuous catalysis beyond the illumination period.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Prof. Philippe Sautet (sautet@ucla.edu).

Materials availability

This study did not generate any new materials.

Data and code availability

Methods and data supporting the findings of this study are available within the article and its Supplemental Methods.

VASP input and output files are available from the lead contact upon request.

AUTHOR CONTRIBUTIONS

P.S. and J.A. conceptualized and supervised the project. Y.L. performed the calculations. G.S. provided experimental data for modeling. All authors together prepared the draft.

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DECLARATION OF INTERESTS

The authors declare no competing financial interest.

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FIGURE TITLES AND LEGENDS

Figure 1. Structure of the Au/a-TiO₂(001) interface model. Au is modeled as a rod along the [010] direction, and TiO₂ is modeled by a p(4×4) 3-layer a-TiO₂(001) slab substrate. Periodic boundary conditions are applied along all directions, only one supercell is shown here.

Figure 2. Phase diagrams of the Au/a-TiO₂(001) interface under ambient conditions. (a) In equilibrium with O₂/H₂, with O/H chemical potentials as descriptors. (b) In equilibrium with H₂O/H₂, with H₂O/H chemical potentials as descriptors. (c) Corresponding structures of the mentioned phases, viewed from the front top. All amounts of adsorbates correspond to a p(4×4) a-TiO₂(001) cell, and adsorbates are underlined by a dashed square box. The black triangle represents a typical H₂O₂ formation experimental condition [p(H₂) = 1.7 bar, p(O₂) = 0.85 bar, T = 275 K]⁴⁴, and the black star represents a CO oxidation experimental condition [p(H₂) = 0.75 bar, p(O₂) = 0.001 bar, T = 353 K], where H₂ is added to prevent *CO₃ formation⁴⁵. Spheres correspond to Au (yellow), Ti (light blue), O (red), and H (white) atoms.

Figure 3. Analysis of the Au/a-TiO₂(001) interface. (a) Pourbaix diagram. The double arrow indicates the reversible electron storage potential range. (b) Bader charge analysis and electron storage mechanism following light illumination (“charging”). Charges are normalized to one p(4×4) a-TiO₂(001) cell.

Figure 4. Thermodynamic study of ORR at the Au/TiO₂ interface. (a) Energy profile of ORR at 0 V vs SHE

(partially charged state). (b) Energy profile of ORR at -0.7 V (fully charged state). (c) Limiting steps and potentials of 4e-/2e-ORR at active sites. (d) Overall picture of ORR at the Au/TiO₂ interface.

Figure 5. Kinetic study of ORR at the Au/TiO₂ interface. Energy profiles comparing 4e-ORR (producing H₂O, black) vs 2e-ORR (producing H₂O₂, red) at the Ti site, starting from *OOH where the branching occurs. (a) At fully charged state (4O_v-phase, potential -0.7 V vs SHE). (b) At partially charged state (4H-phase, potential 0 V vs SHE).

Figure 6. CO₂RR at the Au/TiO₂ interface. (a) Energy profile of CO₂RR at formal reduction potential E⁰ [pH = 7, U = -0.52 V vs SHE], calculated by computational hydrogen electrode. Structures involved in this profile are shown in the table below. (b) Potential dependence of CO₂ adsorption free energy, calculated by surface charging. (c) Energy profile of *CO₂ to *COOH conversion at formal reduction potential, calculated by surface charging.