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Size- and Facet-dependent Behavior of Electron Storage at the Au/anatase TiO₂ Interface under Ambient Conditions from Machine Learning

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Abstract

The interfacial structure and electronic properties of gold (Au) nanoclusters supported on anatase TiO₂ surfaces are key determinants of catalytic and photocatalytic activity for the Au/TiO₂ systems. Here, we present an atomistic study of realistic, ~1.5 nm Au nanoclusters on reconstructed TiO₂(001) and (101) facets in ambient air conditions, bridging the gap between small supported cluster models and experimental catalysts. We focus on the ability of Au/TiO₂ to store photo-generated electrons that can be used later in dark conditions. Leveraging a high-dimensional Au–Ti–O neural-network potential coupled with stochastic surface walking and DFT refinement, we exhaustively sampled atomic configurations over 120,000 minima. Two distinct interfacial motifs emerge—Type (i), with oxygen adsorbed on Ti sites near the Au nanocluster, and Type (ii), with oxygen occupying Au₃ hollow sites. While both motifs stabilize clusters on both facets, Type (ii) is notably more prevalent on (101), giving rise to deeper-lying O 2p states and a larger fraction of fully oxidized Au^{δ+} ($\delta \geq 1$) that can passivate the cluster. In contrast, Type (i) optimally balances neutral Au⁰ and partially oxidized Au^{δ+} ($0 < \delta < 1$), enabling more than 0.90 vacant state per interfacial Au atom and enhancing electron-storage capability. Coupled with facet-dependent behavior and oxidation-state distributions, these findings deliver direct, experimentally relevant design principles for tailoring the electronic functionality of Au/TiO₂ catalysts.

Keywords: gold, titanium oxide, metal-support interaction, electron storage, neural network potential

1. Introduction

The interface between Au nanoclusters and anatase-phase TiO₂ is central to the enhanced catalytic and photocatalytic performance observed in Au/TiO₂ systems^{1–12}. Recently, it was shown that Au nanoparticles on TiO₂ can store photo-generated electrons and provide reactivity in the dark, after illumination has stopped^{13,14}. Anatase TiO₂ exposes primarily the thermodynamically stable (101) surface and the more reactive but less stable (001) surface^{15–18}. Au nanoclusters are typically deposited onto these facets via methods such as impregnation¹⁹, deposition–precipitation^{20–22}, or ligand exchange^{13,23}, often followed by annealing in air. These synthetic procedures give rise to facet-dependent interactions, including local surface reconstruction and interfacial charge transfer, which in turn influence the charge storage ability and overall catalytic behavior^{13,24,25}. As such, elucidating the atomic-scale structure of the Au/anatase TiO₂ interface is essential for understanding catalytic mechanisms and for rational catalyst design.

Despite extensive experimental efforts, the precise nature of the Au/TiO₂ interface remains elusive due to the limited availability of in situ and surface-sensitive structural characterization techniques. Transmission electron microscopy (TEM) has revealed orientation relationships such as Au(111)//TiO₂(101)²³ and Au(111)//TiO₂(001)^{11,19}, with contact angle analysis suggesting stronger Au–support interactions on the (001) facet¹⁹. X-ray photoelectron spectroscopy (XPS) further indicates that while large Au nanoparticles (> ~3 nm) exhibit exclusively metallic Au signals (Au 4f_{7/2} at ~83–84 eV)^{13,21,24–26}, small clusters (< ~3 nm) often display traces of positively charged species (Au⁺, Au³⁺)^{27–29}, suggesting partial oxidation and possible formation of interfacial Au–O bonds. These interfacial oxidation states have been shown to modulate catalytic activity^{29–31}, yet the precise structural origins—how cluster size and interfacial oxygen coordination jointly govern the

emergence of $\text{Au}^{\delta+}$ species—remain unclear. Moreover, for larger nanoparticles, the relatively weak XPS signature of interfacial $\text{Au}^{\delta+}$ can be masked by the overwhelming bulk Au^0 signal, complicating direct experimental observation of these subtle variations in oxidation state.

On the theoretical side, the Au/anatase interface has been widely studied using first-principles methods over the past two decades^{32–36}. Most studies focus on small clusters (typically <15 atoms) adsorbed on unreconstructed anatase surfaces within small unit cells, often neglecting interfacial oxygen and realistic reaction conditions. For example, based on gas-phase structures of Au_n ($n=1–13$) cluster, Wan et al.³⁶ investigated Au_n clusters on unreconstructed $\text{TiO}_2(001)$ and (101) using density functional theory (DFT), and found that Au atoms prefer to bind at coordinatively unsaturated O_{2c} (O atom with O-Ti coordination number (CN) = 2) and Ti_{5c} (Ti atom with Ti-O CN = 5) sites, with stronger interactions on the (001) facet. However, such models omit the effects of interfacial oxidation, which recent works^{11,13,37}—including our previous study on Au rods supported on $\text{TiO}_2(001)$ under ambient conditions ($T=298\text{ K}$, $P(\text{O}_2) = 21\text{ kPa}$)^{13,38}—have shown to be essential for capturing charge transfer and photocatalytic activity.

In this work, we address these gaps by systematically exploring the structural and electronic properties of Au/anatase $\text{TiO}_2(001)$ and (101) interfaces at different cluster sizes (Au_{12} , Au_{30} , Au_{50} , corresponding to diameters up to $\sim 1.5\text{ nm}$), under varying degrees of interfacial oxygen coverage. We especially target ambient air conditions ($T=298\text{ K}$, $P(\text{O}_2) = 21\text{ kPa}$) since key applications of Au/ TiO_2 are for pollutant/poison abatement in air. Leveraging a machine learning potential trained for the Au–Ti–O system, we perform large-scale global structure searches to efficiently sample interfacial configurations, followed by DFT refinement of the most stable structures and electronic structure analysis. Our results reveal how cluster size and oxygen coordination jointly govern interfacial stability and charge redistribution, offering new atomic-level insights into the structure–function relationship of Au/ TiO_2 photocatalysts under realistic conditions.

2. Computational Methods

2.1. SSW-NN Method

The SSW-NN method was utilized extensively to explore the potential energy surface (PES) of Au/anatase $\text{TiO}_2(001)$ and (101) interfaces, which combines the stochastic surface walking (SSW) method^{39,40} for global optimization and a ternary Au–Ti–O global neural network (G-NN) potential in the many-body function corrected neural network (MBNN) architecture⁴¹ for evaluating PES energy. All simulations were performed using the large-scale atomic simulation with neural network potential (LASP) code (<http://www.lasphub.com>)⁴². Compared to conventional DFT calculations, the SSW-NN method significantly speeds up the PES calculations by 3–4 orders of magnitude, making possible the exploration of large-scale PESs on an acceptable time scale.

The Au–Ti–O ternary G-NN potential was generated through iterative self-learning of a vast SSW global PES data set of structures with different compositions and configurations, including AuO_x bulks, slabs and clusters, TiO_x bulks and slabs, Au/ TiO_x interfaces with different x values (See Figure S1). The final training data set consists of a total of 11,479 structures. The as-trained Au–Ti–O G-NN has three atomic feed-forward NN architectures using the hyperbolic tangent function as the activation function. Considering the diversity of the structures in the training dataset, we adopted the NN architecture recommended by the LASP software, which is suitable for describing the complex potential energy surface of the Au–Ti–O system. Each atomic NN architecture contains five fully connected layers, with layer sizes of 299–128–80–80–9 for Au and Ti atoms, and 321–128–80–80–9 for O atoms. The input layer utilizes the power-type structure descriptor (PTSD)⁴³, and the entire model contains a total of 170,603 trainable parameters. Different from the high-dimensional NN architecture proposed by Behler and Parrinello^{44,45}, in which the output of the NN is a single atomic energy, the output in the MBNN potential is a vector utilized in many-body functions, 9 in Au–Ti–O G-NN potential, including single-body, two-body, and three-body functions. The root-mean-square (RMS) errors of energy and force are 3.320 meV per atom and 0.129 eV $\text{\AA}^{-1}$, respectively. All results from the SSW-NN method in this work

have been verified by DFT calculations. The benchmark results are shown in Figure S2. The energy RMS error is 1.02 meV per atom among 1322 structures. The accuracy is good enough for global PES exploration to identify the low-energy minima.

2.2. DFT Calculations

All DFT calculations were performed using the plane-wave Vienna Ab-initio Simulation Package (VASP)⁴⁶. The electron-ion interaction was described by the projected-augmented wave (PAW) method⁴⁷, while the exchange-correlation functional utilized was the generalized gradient approximation with the Perdew-Burke-Ernzerhof (GGA-PBE) functional⁴⁸. To correct for the self-interaction error of Ti 3d electrons, a Hubbard-like repulsion term was added using Dudarev's approach (PBE+U)⁴⁹, with $U_{\text{Ti}} = U - J = 3.5$ eV, determined using linear response⁵⁰. Benchmarking with other functionals (BEEF_vdW+U and SCAN+U) for the electronic structure at the Au/TiO₂ interfaces was also performed (See Table S2), which shows similar results to PBE+U. The dDsC dispersion correction method⁵¹ was used to account for van der Waals forces. For total energy calculations, the first Brillouin zone was sampled using the Monkhorst-Pack scheme, with an automated mesh determined by 25 times the reciprocal lattice vectors for bulk and only the Γ point for surface in the slab model (large unit cells of $19.4 \text{ \AA} \times 31.0 \text{ \AA}$, $23.2 \text{ \AA} \times 31.0 \text{ \AA}$, $20.7 \text{ \AA} \times 23.2 \text{ \AA}$ and $31.0 \text{ \AA} \times 27.1 \text{ \AA}$, corresponding to (5×8) and (6×8) TiO₂(001) surface and (2×6) and (3×7) TiO₂(101) surface, respectively). For electronic structure analysis, a $2 \times 2 \times 1$ k-point mesh was used for the slab model. The kinetic energy cutoff was 450 eV, and the criteria for convergence of the electron density and structure optimization were 5×10^{-6} eV for energy and $0.05 \text{ eV \AA}^{-1}$ for forces.

It should be noted that all crucial minima found by SSW-NN were validated by single-point DFT calculations. To validate the reliability of NN-predicted minima, we evaluated the atomic displacements between the NN-optimized and DFT-optimized minima for 14 interfacial structures (12 interfaces in Table 1 and 2 interfaces in Figure S18). The results in Figure S3 show a small root mean square displacement of $0.060 \text{ \AA}$, suggesting highly similar geometries. In the following sections, all energetics data reported were obtained from DFT calculations without additional notation.

2.3. Modeling of Au/TiO₂ Interface

The Au/TiO₂ interface was modeled by placing Au clusters on the anatase (101) and (001) surfaces (See Figure S4). For the (101) surface, a slab model consisting of two TiO₂ layers was constructed, with the bottom layer fixed at the bulk-truncated positions. For the (001) surface, we adopted the widely accepted ad-molecule reconstruction model⁵², in which rows of bridging oxygen atoms are replaced by TiO₃ groups in a (1×4) periodicity, forming a ridge along the [010] direction (labeled in Figure S4 and Figure 1d). This model contains three TiO₂ layers, with the bottom two layers fixed during structural optimization. In all cases, the Au cluster and the top TiO₂ layer were fully relaxed. The influence of the number of TiO₂ layers in the slabs was evaluated (Table S1 and Figure S6 and S7), confirming the very good reliability of the above models. To accommodate different Au cluster sizes and minimize interactions between periodic images, (2×6) and (3×7) supercells were used for the (101) surface, and (5×8) and (6×8) supercells were used for the (001) surface. A vacuum region of at least $10 \text{ \AA}$ was introduced perpendicular to the slab.

The formation energy of $\text{Au}_n\text{O}_m/\text{TiO}_2$, G_f (eV per Au atom), is calculated by Eq.1:

$$G_f = \frac{1}{n} [G(\text{Au}_n\text{O}_m/\text{TiO}_2) - G(\text{TiO}_2) - n \cdot G(\text{Au}) - m \cdot \mu_{\text{O}}] \quad (\text{Eq. 1})$$

where $G(\text{Au}_n\text{O}_m/\text{TiO}_2)$, $G(\text{TiO}_2)$, $G(\text{Au})$ are the Gibbs free energy of $\text{Au}_n\text{O}_m/\text{TiO}_2$ interface, the corresponding TiO₂ stoichiometric surface global minimum (GM) identified by SSW-NN (See Figure S5) and face-centered cubic bulk Au, respectively. μ_{O} is the oxygen chemical potential from gas O₂ at ambient conditions ($T=298 \text{ K}$, $P(\text{O}_2) = 21 \text{ kPa}$). In computing the free energy, we utilized the DFT total energy to approximate the free energy for solid states because the vibration entropy and the pV term contributions of solid phases are negligibly small; and we corrected the zero-point-energy, thermal and entropy contributions for gas phase O₂ molecule at finite temperatures. The corrections for the gas-phase O₂ (+0.40 eV) free energies are adopted to match the

experimental enthalpy changes for the gas-phase reactions ($\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$). In the following, $\text{Au}_n\text{O}_m/(001)$ and $\text{Au}_n\text{O}_m/(101)$ denote the interfacial structures of an Au_nO_m cluster with n Au atoms and m additional O atoms supported on the anatase $\text{TiO}_2(001)$ and $\text{TiO}_2(101)$ surfaces, respectively.

3. Results

3.1. Thermodynamics of the Au/TiO₂ Interface

To understand the interaction between Au clusters and TiO_2 surfaces, we first employed the SSW-NN method to explore the $\text{Au}_n\text{O}_m/(001)$ and $\text{Au}_n\text{O}_m/(101)$ interfacial structures at three cluster sizes ($n=12, 30, 50$) with varying number of added O (m). To improve the efficiency of structural sampling, O atoms were introduced at

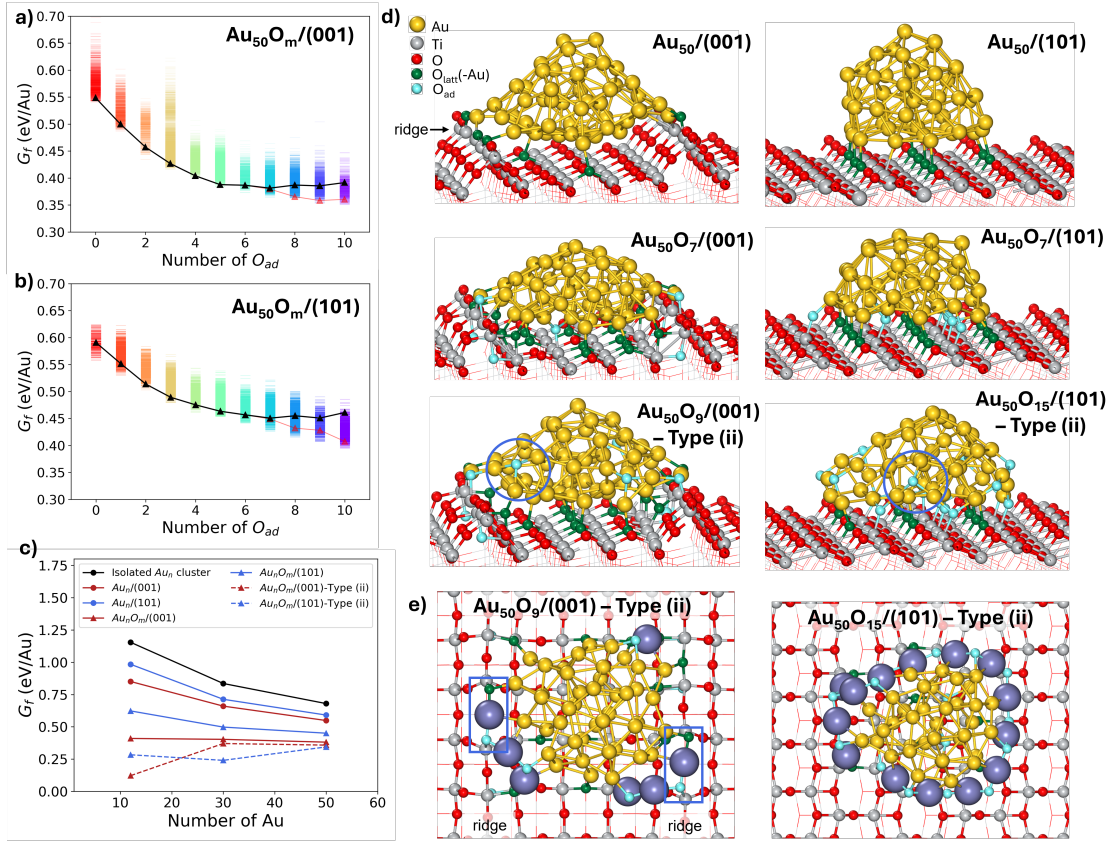


Figure 1. Thermodynamics and interfacial structures of Au/anatase TiO_2 . (a, b) Ensemble formation energy diagram for $\text{Au}_{50}/(001)$ and $\text{Au}_{50}/(101)$ with varying numbers of added O atoms. Sets of horizontal bars represent the formation energy (G_f) of the ensemble of local minima identified via SSW-NN global optimization. Triangles indicate the DFT-calculated G_f of the GM for each composition. Type (i) interface GMs where all O atoms adsorb on the Ti sites are represented by black triangle, and Type (ii) interface GMs where at least one O atom adsorbs at an Au_3 hollow site, interacting exclusively with Au and forming Au-O species are represented by red triangle. (c) G_f of isolated Au_n cluster, $\text{Au}_n/(001)$, $\text{Au}_n/(101)$, $\text{Au}_n\text{O}_m/(001)$, $\text{Au}_n\text{O}_m/(101)$, $\text{Au}_n\text{O}_m/(001)$ -Type (ii) and $\text{Au}_n\text{O}_m/(101)$ -Type (ii) interfacial structures ($n=12, 30$ and 50 , m corresponds to the oxygen content that yields the lowest G_f for each cluster size). (d) Side views of the structures of GM for $\text{Au}_{50}/(001)$, $\text{Au}_{50}\text{O}_7/(001)$, $\text{Au}_{50}\text{O}_9/(001)$ -Type (ii), $\text{Au}_{50}/(101)$, $\text{Au}_{50}\text{O}_7/(101)$ and $\text{Au}_{50}\text{O}_{15}/(101)$ -Type (ii) interfaces. The $\text{O}(-\text{Au}_3)$ species in Type (ii) interface is highlighted in a blue circle. (e) Top views of $\text{Au}_{50}\text{O}_9/(001)$ -Type (ii) and $\text{Au}_{50}\text{O}_{15}/(101)$ -Type (ii) interfaces, with the grey-blue spheres indicating the Au atoms that participate in the $[\text{O}-\text{Au}-\text{O}]$ motifs. The linear $[\text{O}-\text{Au}-\text{O}]$ motifs along the ridge on the (001) surface are highlighted in blue rectangles.

either undercoordinated surface Ti sites (Ti-O CN < 6) near the Au cluster or low-coordinated interfacial Au atoms (Au-Au CN < 4), generating diverse initial $\text{Au}_n\text{O}_m/\text{TiO}_2$ configurations based on the GM structure of the corresponding $\text{Au}_n\text{O}_{m-1}/\text{TiO}_2$ interface. In total, over 120,000 distinct minima were sampled, with at least 2000 minima visited for each composition.

Here we show the formation energy for the ensemble of minima (GM and low energy metastable ensemble (LEME)) for $\text{Au}_{50}\text{O}_m/(001)$ and $\text{Au}_{50}\text{O}_m/(101)$ with varying numbers of added O atoms (m is up to 10, the complete energy diagram for $\text{Au}_{50}\text{O}_m/(101)$ with m up to 16 is shown in Figure S8) in Figure 1a and 1b, respectively (See Figure S8 for the corresponding energy diagram of Au_{12} and Au_{30} on both surfaces). Each set of horizontal bars (distinguished by different colors) represents the formation energies of the ensemble of distinct local minima identified via SSW-NN global optimization for each composition. The formation energies were validated by DFT single-point calculations on the ten lowest-energy minima per composition, with the DFT-confirmed GM marked as triangles in Figures 1a and 1b. SSW-NN yields formation energies that align remarkably well with DFT benchmarks. Two distinct types of $\text{Au}_n\text{O}_m/\text{TiO}_2$ interfaces are observed depending on the adsorption site of the added O atom: (i) structures where all O atoms adsorb on the Ti sites near the Au nanocluster (black triangle in Figure 1a and 1b); and (ii) structures where at least one O atom adsorbs at an Au_3 hollow site (highlighted by a blue circle in Figure 1d), interacting exclusively with Au and forming Au-O species (red triangle in Figure 1a and 1b). It is worth noting that the Type (i) interface forms initially upon O addition, while the Type (ii) interface emerges only after further O incorporation. As shown in Figure 1a and 1b, the transition to the Type (ii) interface occurs when the number of added O atoms reaches seven (Au_{50}O_7) on both (001) and (101) surface. While Type (ii) interfaces are thermodynamically more favorable based on the data in Figures 1a and 1b, it is important to note that, under realistic conditions, Au particles are typically much larger (> 3 nm) than those modeled here (< 2 nm), and they predominantly exhibit metallic Au features in the Au 4f XPS spectra^{13,21}. Therefore, the following discussion focuses on Type (i) interfaces, which are more representative of experimentally relevant systems. In contrast, Type (ii) interfaces may serve as representative models for small clusters with more pronounced Au oxide character. Unless otherwise noted, all structures discussed in the following refer to the Type (i) interface.

The thermostability results of $\text{Au}_n\text{O}_m/\text{TiO}_2$ interface are summarized in Figure 1c, which presents the G_f of GM for Au_n cluster in vacuum, $\text{Au}_n/(001)$, $\text{Au}_n/(101)$, $\text{Au}_n\text{O}_m/(001)$, $\text{Au}_n\text{O}_m/(101)$, $\text{Au}_n\text{O}_m/(001)$ -Type (ii) and $\text{Au}_n\text{O}_m/(101)$ -Type (ii) interfaces ($n=12, 30$ and 50 , m corresponds to the oxygen content that yields the lowest G_f for each cluster size). The most stable Type (i) Au_nO_m clusters on TiO_2 surface in the considered ambient conditions are identified as Au_{12}O_3 , Au_{30}O_5 , and Au_{50}O_7 on the (001) surface, and Au_{12}O_3 , Au_{30}O_7 , and Au_{50}O_7 on the (101) surface (triangle in solid line in Figure 1c). On the other hand, the most stable Type (ii) Au_nO_m clusters with higher content of oxygen on TiO_2 surface are Au_{12}O_7 , Au_{30}O_9 , Au_{50}O_9 on the (001) surface, and Au_{12}O_8 , $\text{Au}_{30}\text{O}_{17}$, $\text{Au}_{50}\text{O}_{15}$ on the (101) surface (triangle in dashed line in Figure 1c). The corresponding interfacial structures are shown in Figure 1d and Figure S9. As illustrated in Figure 1c, our results demonstrate that Au clusters are stabilized on TiO_2 surfaces relative to their respective GM structures in vacuum (see detailed structures in Figure S11). For small Au_{12} clusters, the GM structure in vacuum is a two-dimensional planar configuration featuring Au(111)-like three-fold hollow sites. When interacting with the TiO_2 surface, the GM structures become single-layer clusters with distorted Au(111) characteristics, where interfacial Au atoms bond with lattice oxygen atoms at bridge sites (see $\text{Au}_{12}/(001)$ and $\text{Au}_{12}/(101)$ in Figure S9). In contrast, larger Au_{30} and Au_{50} clusters exhibit multi-layered structures (≥ 3 layers), with the basal layer exhibiting the characteristic Au(111) surface structure.

Upon the introduction of additional oxygen (cyan atoms), Au_{12} clusters become more compact, forming 2–3 atomic layers (e.g., $\text{Au}_{12}\text{O}_3/(001)$ and $\text{Au}_{12}\text{O}_3/(101)$), while Au_{30} and Au_{50} clusters spread more broadly over the surface and adopt flatter morphologies with reduced thickness (e.g., $\text{Au}_{30}\text{O}_5/(001)$, $\text{Au}_{30}\text{O}_7/(101)$, $\text{Au}_{50}\text{O}_7/(001)$, and $\text{Au}_{50}\text{O}_7/(101)$). Interestingly, upon introducing O atoms to the ridge of (001), some Au atoms of the cluster

form linear [O–Au–O] motifs along the ridge (highlighted in blue rectangles in Figure 1e), reducing their Au–Au CN to two or one in the case of Au₅₀, and thereby releasing the surface tensile stress of the TiO₂ support along the [010] direction⁵³. The formation of this [O–Au–O] motif at the ridge can even induce the splitting of the Au cluster with the detachment of one Au atom for smaller sizes (see Au₁₂O₃/(001) and Au₁₂O₇/(001)-Type (ii) in Figure S9). The energy difference between the structures with and without the splitting of Au cluster in Au₁₂O₃/(001) system is -0.60 eV, suggesting that the stress relief achieved by [O–Au–O] insertion provides greater stabilization than detaching a single Au atom from an Au₁₂ cluster.

Notably, Au clusters exhibit greater stabilization on the (001) surface (red solid lines in Figure 1c) than on the (101) surface (blue solid lines). The G_f of Au₁₂, Au₃₀, and Au₅₀ on the (001) surface are 0.85, 0.66 and 0.55 eV, respectively, while the corresponding G_f on the (101) surface are higher (more positive), at 0.98, 0.71 and 0.59 eV, indicative of a less stable cluster. This trend is further supported by the contact angles between the Au clusters and the TiO₂ surfaces (See SI Section 3.3 for the estimation of contact angle), which indicate a stronger interfacial interaction with the (001) surface. As shown in Figure S13, the contact angle of the Au₅₀ cluster on the (101) surface is ~124°. In contrast, the Au₅₀ cluster anchor between adjacent ridges on the (001) surface with reduced contact angles (112°), indicative of stronger adhesion and enhanced interfacial binding^{54,55}. A similar facet-dependent trend in contact angle has also been reported in the in situ TEM experiments by Yuan et al¹⁹. The introduction of interfacial O atoms (triangles in Figure 1c) further stabilizes the Au clusters with decreasing contact angles, for instance, from 112° on Au₅₀/(001) to 96° on Au₅₀O₇/(001), and from 124° on Au₅₀/(101) to 100° on Au₅₀O₇/(101) (Figure S13). Moreover, with further O adsorption, the size dependence of G_f is largely reduced compared to bare Au clusters on the surface (circles in Figure 1c). This effect is particularly pronounced on the (001) surface, where the G_f for Au₁₂, Au₃₀, and Au₅₀ become nearly degenerate (0.41, 0.40, and 0.38 eV, respectively).

It should be noted that Type (ii) interfaces display an inverted stability trend. Our SSW-NN results reveal that Type (ii) interface on (001) becomes less stable as cluster size increases (G_f rising from 0.12 for Au₁₂O₇ to 0.36 eV for Au₅₀O₉), while on the (101) facet the lowest G_f is observed for Au₃₀O₁₇ (0.24 eV). For larger clusters exceeding 1 nm in diameter (Au₃₀ and Au₅₀), the Type (ii) interface is more stable on (101) than on (001), owing to its greater oxygen accommodation (See Figure 1e and Figure S9). For example, the most stable Au₅₀ Type (ii) interfaces on these two surfaces, namely, Au₅₀O₉/(001) and Au₅₀O₁₅/(101), exhibit G_f of 0.36 and 0.34 eV, respectively (Figure 1c). This suggests that (101) is more prone to cluster oxidation than (001). The highly oxidized interfaces, namely Au₁₂O₇/(001)-Type (ii), Au₁₂O₈/(101)-Type (ii) and Au₃₀O₁₇/(101)-Type (ii), all feature distorted Au₆O₅ pentagonal motifs, where a central Au atom resides at or slightly below the pentagon plane (See Figure S10). In particular, Au₃₀O₁₇/(101)-Type (ii) exposes six such pentagons, comprising four Au₆O₅ units and two Au₅O₅ units without the central Au atom.

3.2. Structural Evolution with the Introduction of O Atoms

Our results in Figure 1d show that the introduction of oxygen atoms induces distinct structural modifications on the (001) and (101) surfaces. In the following, we detail the structural evolution of the Au/TiO₂ interface upon O atom incorporation.

On the (001) surface, oxygen incorporation alters the surface reconstruction, as illustrated by the Au₅₀O_m/(001) interfaces in Figure 2a. This figure presents the variation in the coverage of surface Ti atoms with different Ti–O CNs as a function of O content ($m = 0–10$), revealing a three-stage transformation process.

Initially, the pristine ad-molecule reconstructed TiO₂(001) surface contains 0.20 ML of four-coordinated Ti atoms (Ti_{4c}) at the reconstruction ridges and 0.80 ML of five-coordinated Ti atoms (Ti_{5c}). Upon interaction with a bare Au cluster, one Au atom inserts into the ridge, breaking a Ti–O–Ti bond (Figure 2b, top left), and forming a three-coordinated Ti atom (Ti_{3c}). In the first stage of O incorporation, the added O atom binds to the Ti_{3c}, forming a linear [O–Au–O] structure along the ridge (Figure 2b, top right), converting Ti_{3c} into Ti_{4c} (Ti_{3c}

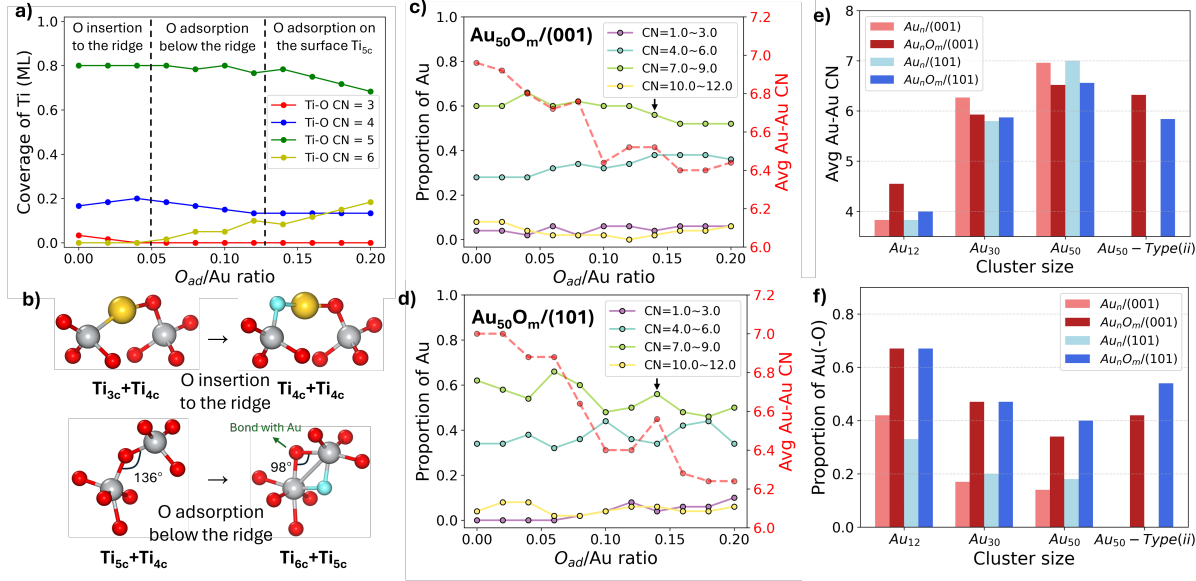


Figure 2. Structural evolution of Au clusters on TiO₂ with the introduction of O atoms. (a) Variation in the coverage of surface Ti atoms with different Ti-O CNs as a function of O content ($m = 0-10$) on Au₅₀O_m/(001) interface. (b) Modification of the reconstructed (001) surface induced by the introduction of extra O atoms. (c,d) Variation of Au-Au CN with increasing O coverage on Au₅₀O_m/(001) and Au₅₀O_m/(101) interfaces. The y-axis on the left is the proportion of Au at the corresponding Au-Au CN (purple: 1~3, cyan: 4~6, green: 7~9, and yellow: 10~12). The y-axis on the right is the average Au-Au CN for the Au₅₀ cluster (red). The arrows denote to the most stable interfaces. (e, f) Au-Au CN and proportion of Au(-O) of the GM of Au/TiO₂ interfaces at different sizes.

coverage decreases from 0.03 to 0 ML, while Ti_{4c} increases from 0.17 to 0.20 ML; see Figure 2a). In the second stage, O atoms adsorb below the ridge, bonding to the bottom-right of Ti_{4c} atoms. This results in the transformation of bottom Ti_{5c} and top Ti_{4c} into Ti_{6c} and Ti_{5c}, respectively (Ti_{4c} decreases from 0.17 to 0.13 ML, and Ti_{6c} increases from 0 to 0.08 ML). As shown in Figure 2b (bottom), the distance between top and bottom Ti atoms at the ridge decreases from ~3.65 Å to ~3.00 Å, and the Ti-O-Ti angle on the ridge side decreases from ~136° to ~98°. These geometric changes result in the protrusion of a side oxygen atom, which forms a bond with the Au cluster (green arrow in Figure 2b). In the final stage, additional O atoms adsorb atop Ti_{5c} atoms on the terrace beneath the Au cluster, completing their coordination shells and forming Ti_{6c} sites. This is evidenced by the increasing Ti_{6c} coverage and decreasing Ti_{5c} coverage in Figure 2a. Each adsorbed O atom on a Ti_{5c} site also forms two bonds with the basal layer of the Au cluster, establishing Au-O-Au bridges at the interface (Au₅₀O₇/(001) in Figure 1d). During this process, the TiO₂ surface structure remains unchanged, with no further structural modification occurring. In contrast, the structurally stable (101) surface—with 0.50 ML each of Ti_{5c} and Ti_{6c}—exhibits no surface reconstruction upon O incorporation. All additional O atoms preferentially adsorb on top of Ti_{5c} sites at the interface with the cluster (see Ti-O CN data for the (101) surface in Figure S14). The adsorbed O atoms also attach to the basal layer of the Au cluster: those at the edge form one or two Au-O bonds, while those directly beneath the cluster form two Au-O bonds.

One step further, we analyzed the variation in the Au-Au CNs at Au/TiO₂ interface as a function of O content. The results of Au₅₀O_m/(001) and Au₅₀O_m/(101) interfaces are shown in Figure 2c and 2d, while those for the other interfaces are provided in Figure S15 and S16. In Figure 2c and 2d, the left y-axis indicates the proportion of Au atoms corresponding to specific Au-Au CN ranges (purple: 1~3, cyan: 4~6, green: 7~9, and yellow: 10~12), while the right y-axis shows the average Au-Au CN of the Au₅₀ cluster (red dashed line). The most stable interfaces, Au₅₀O₇/(001) and Au₅₀O₇/(101), are marked with arrows. For both surfaces, the increasing O content

leads to a reduction in the average Au-Au CN: from 6.96 to 6.52 for $\text{Au}_{50}/(001)$ to $\text{Au}_{50}\text{O}_7/(001)$, and from 7.00 to 6.56 for $\text{Au}_{50}/(101)$ to $\text{Au}_{50}\text{O}_7/(101)$. This decrease primarily arises from an increase in the number of Au atoms with 4–6 Au–Au CNs and a decrease in those with 7–9 CNs.

Figure 2e and 2f summarize the average Au–Au CN and proportion of Au atoms bonded to O (denoted as Au(–O)) for various Au/TiO₂ interfaces. Unlike Au_{50} , smaller clusters exhibit different trends. For instance, the Au–Au CN increases with O addition on $\text{Au}_{12}/(001)$, $\text{Au}_{12}/(101)$ and $\text{Au}_{30}/(101)$ interfaces (from 3.83, 3.83 and 4.00 to 4.55, 4.00 and 5.87, respectively), whereas it decreases on the other interfaces (from 6.27, 6.96 and 7.00 to 5.93, 6.52 and 6.56 for $\text{Au}_{30}/(001)$, $\text{Au}_{50}/(001)$ and $\text{Au}_{50}/(101)$, respectively). This is because small clusters tend to wet the TiO₂ surfaces, exhibiting single-layer configuration without additional O atoms, while the additional O atoms lift the cluster into structures with 2–3 layers (Figure S9). However, larger clusters become less compact since more interfacial Au sites are needed to accommodate the higher concentration of interfacial O atoms.

Figure 2e and 2f further show that increasing cluster size results in more bulk-like Au structures, reflected by higher average Au–Au CNs and a lower proportion of Au(–O) species. Our SSW-NN simulations (Figure S9 and S10) confirm that for Type (ii) interfaces, Au_{12} and Au_{30} clusters are too small to exhibit dominant metallic characteristics, while Au_{50} clusters can adopt metallic-like features, as exemplified by the $\text{Au}_{50}\text{O}_9/(001)$ and $\text{Au}_{50}\text{O}_{15}/(101)$ configurations (Figures 1d and 1e) identified in the SSW-NN search. Comparative analysis of Au_{50} -Type (i) and Type (ii) interfaces in Figures 2e and 2f reveals that Type (ii) configurations exhibit lower Au–Au CNs (6.32 and 5.84 on the (001) and (101) surfaces, respectively) and higher proportions of Au(–O) species (0.42 and 0.54) than their Type (i) counterparts. Notably, the Au_{50} -Type (ii)/(101) interface exhibits stronger interactions with O species, leading to a more significant reduction in Au–Au CN and an increase in Au(–O) content. For the $\text{Au}_{50}\text{O}_9/(001)$ -Type (ii) interface, three oxygen atoms occupy Au_3 hollow sites at the cluster's periphery adjacent to the ridge, pairing with ridge O atoms to form [O–Au–O] motifs (the Au atoms involved are shown as grey-blue spheres in Figure 1e). In contrast, the $\text{Au}_{50}\text{O}_{15}/(101)$ -Type (ii) interface features six oxygens coordinated to Au_3 hollow sites, which, together with O atoms adsorbed on Ti_{5c} sites and lattice O atoms at bridge positions, create a continuous [O–Au–O] chain encircling the edge of cluster (Figure 1e). Notably, similar [O–Au–O] motifs have also been observed in surface science experiments, where ozone exposure on single-crystal Au surfaces leads to the formation of such chain structures^{56–59}. These experimental observations, reported via scanning tunneling microscopy (STM)^{57,58} and high-resolution electron energy loss spectroscopy (HREELS)⁵⁶, support the structural motifs we observe in our simulations.

3.3. Electronic Structure

We are now in a position to elaborate on how the Au cluster size and the presence of oxygen species influence the electronic structure of the Au/TiO₂ interface. To this end, we analyzed the density of states (DOS) for 14 representative Au/TiO₂ interfaces, including seven $\text{Au}_n\text{O}_m/(101)$ and seven $\text{Au}_n\text{O}_m/(001)$ configurations with varying cluster sizes and oxygen contents (Type (ii) interfaces are also included). Table 1 and Table S3 summarizes the structural and electronic properties of the 12 most stable Type (i) and Type (ii) interfaces, as identified by SSW-NN, across different cluster sizes and TiO₂ surfaces. The projected DOS for selected interfaces— $\text{Au}_{12}\text{O}_3/(001)$, $\text{Au}_{30}\text{O}_5/(001)$, $\text{Au}_{50}\text{O}_7/(001)$, $\text{Au}_{50}\text{O}_9/(001)$ -Type (ii), $\text{Au}_{50}\text{O}_7/(101)$, and $\text{Au}_{50}\text{O}_{15}/(101)$ -Type (ii)—are shown in Figure 3a. The atomic structures of Type (i) and Type (ii) interfaces are presented in Figure 1d and Figure S9, respectively. The DOS of the remaining interfaces are also provided in Figure S17.

Figure 3a displays the projected DOS contributions from all Au (yellow), Ti (blue), and O (green), averaged over the corresponding atoms. It also highlights the DOS of interfacial O atoms (int-O, red)—defined as surface oxygen atoms bonded to Au—including adsorbed adatom oxygen on Ti_{5c} sites (O(– Ti_{5c}), orange), oxygen coordinated to Au_3 hollow sites (O(– Au_3), purple), and lattice O from the TiO₂ framework (O_{int-latt}, pristine O atoms on TiO₂ surface and the inserted O atom along the ridge of (001) surface shown in Figure 2b). The numbers

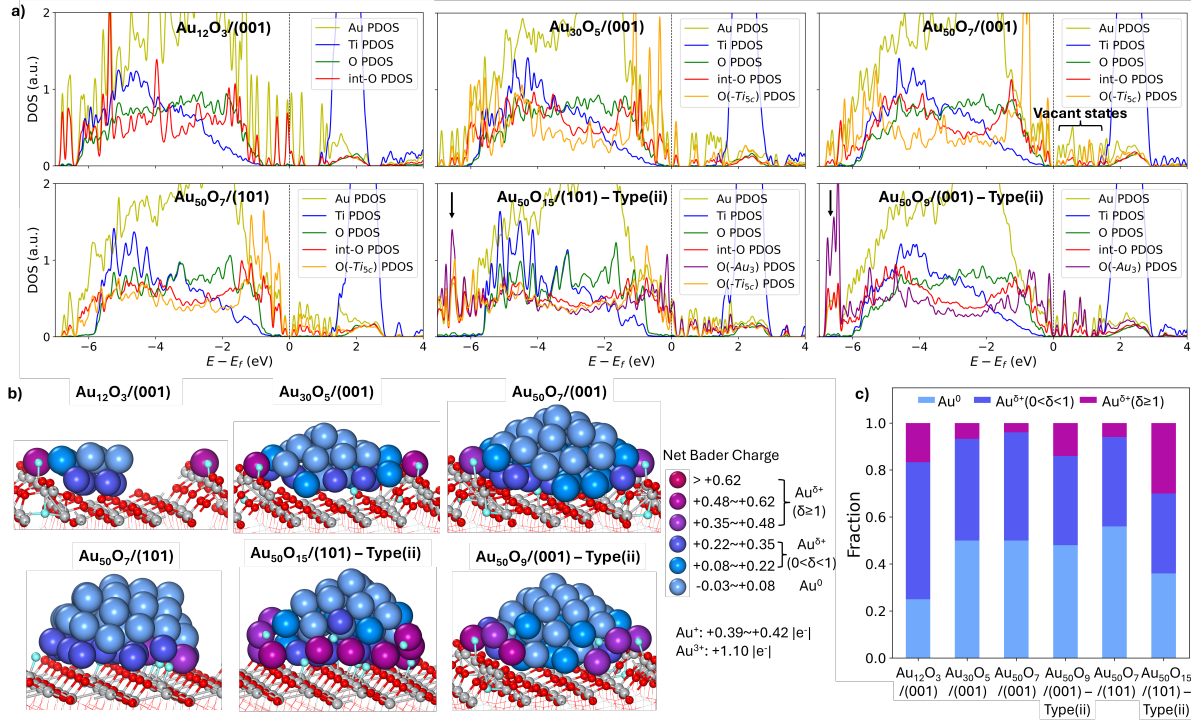


Figure 3. Electronic structure of Au/TiO₂ interface. (a) The projected DOS of Au₁₂O₃/(001), Au₃₀O₅/(001), Au₅₀O₇/(001), Au₅₀O₉/(001)-Type (ii), Au₅₀O₇/(101), Au₅₀O₁₅/(101)-Type (ii) interfaces. All Au, Ti, O atoms, interfacial O, O(-Ti_{5c}) and O(-Au₃) atoms are represented by yellow, blue, green, red, orange and purple lines, respectively. The y-axis is the DOS averaged over the corresponding atoms. (b) Net Bader charge distribution of Au atoms in Au/TiO₂ interfaces (side view). The cyan small ball represents the added O atom. (c) The fraction of Au atoms in Au⁰, Au^{δ+} (0 < δ < 1) and Au^{δ+} (δ ≥ 1) oxidation states in different Au/TiO₂ interfaces based on the net Bader charge analysis.

of vacant states between the Fermi level and the conduction band minimum (CBM) of TiO₂ extracted from DOS are listed in Table 1. These values reflect the electron storage capacity, a key property for post-illumination photocatalysts^{60,61}. The top panel of Figure 3a presents the projected DOS for Au/(001) interfaces with increasing cluster sizes (Au₁₂, Au₃₀, and Au₅₀). The results indicate that larger Au clusters generate more vacant states — 0.50, 0.78 and 0.91 vacant states per interfacial Au (int-Au, defined as the Au atoms bonded to Ti or O atoms), respectively — implying an enhanced capacity to accommodate electrons. This trend arises from the broader electronic bands provided by larger Au clusters, which increases the density of available states. In the case of the smaller Au₁₂ cluster, the int-O species is originated from the TiO₂ framework, which can hardly provide abundant low-lying vacant states near the Fermi level. Moreover, the adsorption of O(-Ti_{5c}), which is capable of inducing substantial charge transfer (as reflected by the orange lines in Figure 3a), is thermodynamically unfavorable on this interface. The ratio of the number of O(-Ti_{5c}) atoms to the number of int-Au, $r(\text{O}(-\text{Ti}_{5c}))$, is zero in Au₁₂O₃/(001) as shown in Table S3. Our calculations further show that bare Au clusters on TiO₂ surfaces such as Au₃₀/(001) and Au₃₀/(101), do not exhibit any vacant states near the Fermi level (See Figure S18). However, upon adsorption of O(-Ti_{5c}), the Au₃₀O₅/(001) and Au₃₀O₇/(101) interfaces display 0.78 and 1.07 vacant states per int-Au, respectively. These findings reinforce the critical role of O(-Ti_{5c}) in creating interfacial vacant states, consistent with our previous work^{13,38}.

Table 1. Structural and electronic properties of Au/TiO₂ interface. The most stable structures of Type (i) and Type (ii) interfaces with varying cluster sizes and TiO₂ surfaces are listed. The listed data include bond-order-like coordination number of Au-Au (Au-Au CN_{BO}), ratios of the number of Au atoms with Au-O CN ≥ 2 to the number of int-Au ($r[\text{Au}(\text{Au-O CN} \geq 2)]$), fractions of Au⁰, Au ^{δ^+} (0< δ <1) and Au ^{δ^+} ($\delta \geq 1$) atoms ($f(\text{Au}^0)$, $f(\text{Au}^{\delta^+}, 0 < \delta < 1)$ and $f(\text{Au}^{\delta^+}, \delta \geq 1)$), ratio of the number of Au ^{δ^+} (0< δ <1) atoms to the total number of oxidized Au atoms ($r(\text{Au}^{\delta^+}, 0 < \delta < 1)$), the number of vacant states per int-Au (N).

Interface	Au-Au CN _{BO}	$r[\text{Au}(\text{Au-O CN} \geq 2)]$	$f(\text{Au}^0)$	$f(\text{Au}^{\delta^+}, 0 < \delta < 1)$	$f(\text{Au}^{\delta^+}, \delta \geq 1)$	$r(\text{Au}^{\delta^+}, 0 < \delta < 1)$	N(vacant states per int-Au)
Au ₁₂ O ₃ /(101)	3.86	0.13	0.33	0.25	0.42	0.38	0.75
Au ₁₂ O ₈ /(101) -Type (ii)	2.70	0.91	0.00	0.17	0.83	0.17	0.55
Au ₃₀ O ₇ /(101)	5.51	0.40	0.47	0.33	0.20	0.63	1.07
Au ₃₀ O ₁₇ /(101) -Type (ii)	3.97	0.96	0.00	0.23	0.77	0.23	0.67
Au ₅₀ O ₇ /(101)	6.05	0.15	0.56	0.38	0.06	0.86	1.00
Au ₅₀ O ₁₅ /(101) -Type (ii)	5.53	0.54	0.36	0.34	0.30	0.53	0.64
Au ₁₂ O ₃ /(001)	4.06	0.25	0.25	0.58	0.17	0.78	0.50
Au ₁₂ O ₇ /(001) -Type (ii)	1.91	1.00	0.00	0.09	0.92	0.09	0.18
Au ₃₀ O ₅ /(001)	5.48	0.27	0.50	0.43	0.07	0.87	0.78
Au ₃₀ O ₉ /(001) -Type (ii)	5.18	0.40	0.27	0.47	0.27	0.64	0.80
Au ₅₀ O ₇ /(001)	6.17	0.14	0.50	0.46	0.04	0.92	0.91
Au ₅₀ O ₉ /(001) -Type (ii)	6.01	0.30	0.48	0.38	0.14	0.73	0.78

In the present study, we also identified another distinct type of oxygen species, O(-Au₃), associated with Type (ii) interfaces. Given the thermodynamic stability of Type (ii) interfaces for small Au clusters (< 2 nm), we further examined their electronic structure for comparison (bottom panel in Figure 3a). Obviously, Type (ii) interfaces exhibit fewer vacant states (0.78 and 0.64 vacant states per int-Au for Au₅₀O₉/(001)-Type (ii) and Au₅₀O₁₅/(101)-Type (ii), respectively) compared to Type (i) interfaces (0.91 and 1.00 vacant states per int-Au for Au₅₀O₇/(001) and Au₅₀O₇/(101), respectively).

While both types of interfacial oxygen species induce charge transfer from neighboring Au atoms, their impact on the electronic structure is notably distinct. O(-Ti_{5c}) often bridge between Ti and Au atoms, and their 2p states appear close to the Fermi level. These O species accept electrons from Au, yet the resulting hybridized states introduce new unoccupied orbitals near the Fermi level, thereby increasing the density of vacant states between the Fermi level and the CBM. In contrast, O(-Au₃) species exhibit a different electronic signature. Their 2p states lie significantly deeper in energy (-6.0 eV lower than the Fermi level as indicated by the arrows Figure 3a), and although they also receive electrons from adjacent Au atoms, the resulting bonding states do not contribute near-fermi-level features. Instead, this interaction leads to a reduction of Au-derived states near the Fermi level, effectively passivating the Au cluster and decreasing the density of interfacial vacant states. Interestingly, for the Au₅₀O₁₅/(101) interface, O(-Ti_{5c}) species also contribute to deep energy states. This is

attributed to the formation of an [O–Au–O] chain-like structure, in which O(-Ti_{5c}) and O(-Au₃) atoms cooperate at the periphery of the Au cluster (Figure 1e).

In support of these findings, the net Bader charge distribution of Au atoms across various Au/TiO₂ interfaces is presented in Figure 3b and further quantified in Figure 3c and Table 1. Importantly, the Bader analysis distinguishes three classes of Au atoms: (i) neutral Au⁰ with minimal charge transfer ($-0.03 \sim +0.08$ |e⁻|), (ii) partially oxidized Au^{δ+} ($0 < \delta < 1$) with moderate electron loss ($+0.08 \sim +0.35$ |e⁻|), and (iii) fully oxidized Au^{δ+} ($\delta \geq 1$) atoms ($> +0.35$ |e⁻|, the net Bader charge for Au⁺ and Au³⁺ in the Au₂O and Au₂O₃ bulk structures are $+0.39 \sim +0.42$ |e⁻| and $+1.10$ |e⁻|, respectively). As illustrated in Figure 3b and Figure S19, Au⁰ atoms are generally located away from the surface and lack direct bonding to interfacial species. In contrast, Au^{δ+} ($0 < \delta < 1$) atoms are often bonded to the TiO₂ surface via interactions with lattice oxygen or adsorbed oxygen species such as O(-Ti_{5c}). Fully oxidized Au^{δ+} ($\delta \geq 1$) atoms are predominantly found in linear [O–Au–O] motifs, including those formed by Au atoms inserted along the (001) surface ridge or coordinated with O(-Au₃) species. This is consistent with prior theoretical studies^{31,62,63} showing that Au atoms coordinated to two O atoms carry a net charge of roughly $+0.5$ |e⁻|.

Figure 3c reveals systematic oxidation of interfacial Au atoms in the presence of reactive oxygen species. Specifically, the fraction of Au^{δ+} ($\delta \geq 1$) atoms increases in Type (ii) interfaces (e.g., Au₅₀O₉/(001)-Type (ii) and Au₅₀O₁₅/(101)-Type (ii)), which contain O(-Au₃) species forming stable [O–Au–O] configurations. These interfaces exhibit up to 30% of Au atoms in the high oxidation state range, in stark contrast to Type (i) interfaces such as Au₃₀O₅/(001) or Au₅₀O₇/(001), where the majority of Au atoms remain nearly neutral ($\sim 50\%$ Au⁰ and $\sim 45\%$ Au^{δ+} ($0 < \delta < 1$)). Notably, the (101) surface appears to promote a higher proportion of Au^{δ+} ($\delta \geq 1$) species compared to the (001) surface, consistent with our thermodynamic analysis showing that more oxygen can be accommodated at Au/(101) Type (ii) interfaces. The trend observed in the net Bader charge distribution for the Au₅₀-Type (ii) interface aligns well with experimental XPS results for Au/TiO₂ catalysts with small cluster sizes (~ 1.5 nm), which report a higher abundance of Au⁰ on Au/TiO₂(001) (69.92% Au⁰, 25.44% Au⁺, and 4.64% Au³⁺) than on Au/TiO₂(101) (51.55% Au⁰, 39.66% Au⁺, and 8.79% Au³⁺)²⁸. This trend is also reflected in the projected DOS features (Figure 3a): the presence of fully oxidized Au correlates with a suppression of Au-derived states near the Fermi level, especially in Type (ii) systems where charge is strongly localized onto deep-lying O 2p states.

4. Discussion

4.1. Structural Origin of Electron Storage Performance

To elucidate how the oxidation state of Au influences the emergence of unoccupied states near the Fermi level, we constructed a contour map (Figure 4a) showing the number of vacant states per int-Au atom as a function of the fractions of Au⁰ and Au^{δ+} ($0 < \delta < 1$) species in the total cluster. Twelve representative Au/TiO₂ interfaces from Table 1 were analyzed. Our results reveal that both a high proportion of metallic Au⁰ and partially oxidized Au^{δ+} ($0 < \delta < 1$) species enhance the formation of available vacant states (0.77~1.07 vacant states per int-Au for Au₃₀O₅/(001), Au₃₀O₇/(101), Au₅₀O₇/(001), Au₅₀O₉/(001)-Type (ii) and Au₅₀O₇/(101)), with optimal fractions of approximately $50 \pm 5\%$ Au⁰ and $40 \pm 5\%$ Au^{δ+} ($0 < \delta < 1$). Conversely, insufficient amounts of either species suppress these vacant states (< 0.70 vacant states per int-Au for Au₁₂O₃/(001), Au₁₂O₇/(001)-Type (ii), Au₁₂O₃/(101), Au₁₂O₈/(101)-Type (ii), Au₃₀O₉/(001)-Type (ii), Au₃₀O₁₇/(101)-Type (ii) and Au₅₀O₁₅/(101)-Type (ii)). The low amount of both Au⁰ and Au^{δ+} ($0 < \delta < 1$) species in Figure 4a (Au₁₂O₇/(001)-Type (ii), Au₁₂O₈/(101)-Type (ii) and Au₃₀O₁₇/(101)-Type (ii)) suggests the high abundance of strongly cationic Au^{δ+} ($\delta \geq 1$) species, which is unfavorable for electron storage (< 0.55 vacant states per int-Au).

One step further, we found that the Au⁰ fraction correlates positively with the Au–Au connectivity (represented by the bond-order-like coordination number, Au–Au CN_{BO}, in Figure 4b, See SI Section 1.2 for the calculation of CN_{BO}), indicating that larger, more compact clusters offer greater electronic density for charge redistribution.

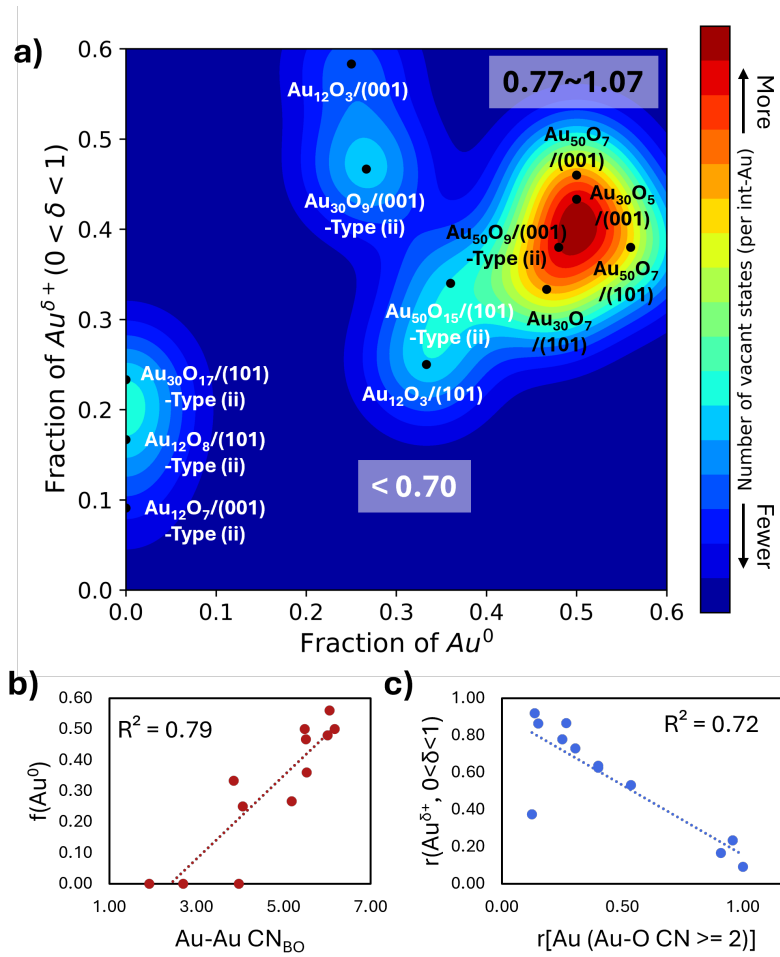


Figure 4. (a) Contour map for the number of vacant states per int-Au atom as a function of the fractions of Au^0 and $\text{Au}^{\delta+}$ ($0 < \delta < 1$) species. (b) The Au^0 fraction ($f(\text{Au}^0)$) correlates positively with the $\text{Au-Au CN}_{\text{BO}}$. (c) The ratio of $\text{Au}^{\delta+}$ ($0 < \delta < 1$) atoms to the total oxidized Au population ($r(\text{Au}^{\delta+}, 0 < \delta < 1)$) correlates negatively with the proportion of int-Au atoms coordinated to two or more O atoms ($r[\text{Au}(\text{Au-O CN} \geq 2)]$).

In contrast, the ratio of $\text{Au}^{\delta+}$ ($0 < \delta < 1$) atoms to the total oxidized Au population ($r(\text{Au}^{\delta+}, 0 < \delta < 1)$) correlates negatively with the proportion of int-Au atoms bonded to two or more O atoms ($r[\text{Au}(\text{Au-O CN} \geq 2)]$, Figure 4c). This suggests that to promote unoccupied states without passivating the cluster, each int-Au atom should maintain an Au-O CN of one.

Indeed, as shown in Table 1, interfaces on the (001) surface exhibit higher $r(\text{Au}^{\delta+}, 0 < \delta < 1)$ than those on (101) (e.g., 0.92 vs. 0.86 for Au_{50}O_7), driven by a larger lattice-oxygen contribution ($r(\text{O}_{\text{int-latt}})$) that offsets the lower density of $\text{O}(\text{-Ti}_{5c})$ sites. Although $\text{O}(\text{-Ti}_{5c})$ species can facilitate charge transfer and generate vacant states, their overabundance on the (101) surface promotes the formation of $[\text{O-Au-O}]$ motifs that passivate the cluster and suppress vacant state formation (see the PDOS of $\text{Au}_{50}\text{O}_{15}/(001)$ -Type (ii) in Figure 3a). In contrast, the sparse distribution of $\text{O}(\text{-Ti}_{5c})$ on the (001) terraces limits higher Au-O coordination, thereby favoring the emergence of vacant states near the Fermi level. This balance also explains why $\text{Au}_{50}\text{O}_7/(001)$ and $\text{Au}_{50}\text{O}_7/(101)$ host similar numbers of vacant states despite the higher $r(\text{O}(\text{-Ti}_{5c}))$ (0.05 vs. 0.35 shown in Table S3) in the latter.

Our results in Figure 4a indicate that both Au^0 and $\text{Au}^{\delta+}$ ($0 < \delta < 1$) are important for electron storage, a key property for photocatalytic activity, particularly in post-illumination conditions^{60,61}. The fraction of Au^0 is

positively correlated with the Au-Au CN_{BO}, and thus with the cluster size (Figure 4b). The size effect towards the electron storage and photocatalytic activity of supported Au nanoparticles on TiO₂ has been extensively studied in experiments^{10,64–67}. Subramanian et al.⁶⁴ reported that after UV-irradiation the Fermi level energy of Au/TiO₂ increased with decreasing Au particle size (3~8 nm) when 3-mercaptopropionic acid was used as a bifunctional linker in a low polar toluene-ethanol mixed solvent, which was attributed to the quantum size effect of ultrasmall Au nanoparticles. It should be noted that higher Fermi level after photo irradiation does not imply better electron storage performance. Our DOS analysis (Table 1) demonstrates worse electron storage capacity for smaller clusters owing to their decreased metallic character and insufficient number of Au⁰ atoms required to reach a large population of available vacant states. For example, four Au₁₂ clusters (Au₁₂O₃/(001), Au₁₂O₇/(001)-Type (ii), Au₁₂O₃/(101), Au₁₂O₈/(101)-Type (ii)) display a Au⁰ fraction $f(\text{Au}^0)$ values below 0.35, with fewer than 0.75 vacant states per int-Au. In practice, TiO₂ surfaces are often hydrated or covered with hydroxyl groups under photocatalytic conditions^{68,69}, which can modify the electronic structure of the Au/TiO₂ interface. Kiyonaga et al.⁷⁰ combined voltammetry measurements in water using S/S²⁻ as a redox probe, photoluminescence analysis and DFT calculations to show that the Fermi level of Au/TiO₂ at the photostationary state increases with particle size (3~13 nm), due to the relative decrease of the stabilization energy from solvation in water and the increased efficiency of the electron transfer from TiO₂ to Au in larger nanoparticles. Accordingly, we propose that the electron storage capacity of larger nanoparticles is superior to small ones, owing to both a higher post-illumination Fermi level and a greater density of vacant states. However, electron storage alone does not fully determine photocatalytic activity. While larger clusters can accumulate more electrons and facilitate interfacial charge transfer from TiO₂, overly large particles may suffer from reduced surface-to-volume ratios⁶⁶ and strong metal–support interactions (SMSI)⁷¹, which limit the number of active sites. As a result, the optimal photocatalytic activity is generally observed at intermediate particle sizes (~5 nm)^{65,66}.

As for the fraction of Au^{δ+} ($0 < \delta < 1$), our results show that it can be tuned by the interfacial environment, such as the exposed crystal facet of TiO₂. Since the (001) surface is more reactive, this develops more binding between Au atoms of the cluster and O atoms from the support (as seen by number of green O atoms on figure 1d and the less positive formation free energy G_f in Figure 1c compared to (101)) and as a result the Au supported cluster has a lower tendency toward oxidation (9 O atoms in the Type(ii) structure of Au₅₀ on (001) vs 15 O on (101)) and towards the formation of strongly cationic gold (Au^{δ+}, $\delta \geq 1$), a species detrimental for electron storage (Figure 1d). Therefore, the Au cluster on the (001) surface can reach the optimal amount of metallic and interfacial Au^{δ+} ($0 < \delta < 1$) species to maximize the electron storage capacity (Figure 4a). Son et al.¹³ investigated Au/TiO₂ catalysts with well-defined surface terminations, employing Au nanoparticles of ~9.5 nm in diameter and reported that Au/TiO₂(001) exhibits the highest specific capacitance of 74.25 mC/g, corresponding to an estimated ~130 electrons stored per Au nanoparticle (See SI Section 5.3 for the estimation), whereas Au/TiO₂(101) only displayed 24.64 mC/g. They further demonstrated that photocharged Au/TiO₂ particles could catalyze reactions in the dark, including H₂O₂ formation and methylene blue degradation, with Au/TiO₂(001) being the most active catalyst. To connect with our calculations, we extrapolated the theoretical storage to the experimental size level (~9.5 nm) based on our results that Au₅₀O₇/(001) interface has 0.91 vacant states per int-Au atom between the Fermi level and the CBM of TiO₂ (Table 1). From this, our theoretical predictions indicate that a ~9.5 nm Au cluster can store approximately 80 electrons (details are in SI Section 5.3), in good agreement with the experimental result. Moreover, their Au 4f XPS measurements revealed a +0.2 eV shift in the Au⁰ peak for the Au/TiO₂(001) catalyst, whereas no such shift was observed for Au/TiO₂(101). This observation aligns with our data in Table 1, where the Au₅₀O₇/(001) interface exhibits a higher fraction of partially oxidized Au^{δ+} ($0 < \delta < 1$) species, at 0.46, compared to 0.38 for Au₅₀O₇/(101).

In summary, both metallic Au⁰ and partially oxidized Au^{δ+} ($0 < \delta < 1$) play key roles in electron storage and photocatalytic activity of Au/TiO₂. Based on our results and previous experiments, larger clusters can store more electrons, but the best catalytic performance is usually found at medium sizes (~5 nm), especially when the

interface favors more $\text{Au}^{\delta+}$ ($0 < \delta < 1$) species, such as on the $\text{TiO}_2(001)$ surface with its lower Au cluster overoxidation tendency.

4.2. Advancing Metal–Support Modeling Beyond Idealized Systems

At this stage, we turn to discuss the advantages of our workflow for modeling supported metal catalysts. Most previous computational studies on supported metal catalysts have relied on simplified models, such as 1D periodic rods^{31,38,72} or small clusters (< 15 atoms)^{32–36} supported on perfect substrate slabs. While these models provide useful insights, they fail to capture the realistic structural complexity of supported nanoparticles, including size-dependent morphologies and dynamic reconstruction. Moreover, the high cost of DFT limits simulations to only a few tens of atoms, making it difficult to study nanoparticles at experimentally relevant sizes. In this work we highlight the novelty of combining machine-learning potential with global PES search strategies. This framework extends near-DFT accuracy to systems with hundreds to thousands of atoms, enables unbiased sampling of interfacial structures, and allows for dynamical simulations that reveal restructuring⁷³ and adsorbate-induced transformations^{37,74}. When coupled with DFT refinement for key electronic properties, this approach provides a powerful way to explore the structure–function relationships of supported metal catalysts beyond the reach of conventional methods.

Importantly, extensive experimental studies have shown that support effects, such as strong metal–support interactions^{55,75} and interfacial charge transfer^{8,9,12}, play a central role in catalytic performance. Therefore, explicitly including the metal–support interface in atomistic modeling provides a more reliable foundation for understanding catalytic mechanisms. Although in the present work we only varied the O coverage and did not explicitly include H_2O or OH groups on the TiO_2 surface, the models and trends obtained here can serve as a solid foundation for future studies that incorporate hydroxyl species to further unravel their impact on interfacial structure and reactivity.

5. Conclusion

By employing the combination of SSW-NN global optimization and DFT refinement approach to systematically explore the Au_nO_m ($n=12, 30, 50$) clusters on reconstructed $\text{TiO}_2(001)$ and $\text{TiO}_2(101)$ facets, we achieve a comprehensive understanding of the structural and electronic properties of the Au/ TiO_2 interfaces in ambient air conditions. Key conclusions include:

- (i) Au clusters exhibit stronger binding and enhanced wetting on the reconstructed $\text{TiO}_2(001)$ surface compared to $\text{TiO}_2(101)$, reflected in lower (more stable) formation energies and smaller contact angles. Oxygen incorporation further stabilizes clusters, particularly on (001), where E_f values is constant across cluster sizes.
- (ii) Two interface motifs emerge with increasing interfacial O content: Type (i) interface features oxygen bound to Au and Ti sites. These interfaces are favored for larger clusters and confer an optimal balance of electronic states, enhancing vacant-state availability. Type (ii) interface involves oxygen occupying Au_3 hollow sites. This motif is more readily formed on the (101) facet and predominates for sub-nanometer clusters, where the resulting deeper-lying O 2p states tend to passivate the Au core.
- (iii) Achieving an optimal balance of Au oxidation states ($\sim 50 \pm 5\%$ Au^0 and $\sim 40 \pm 5\%$ $\text{Au}^{\delta+}$ ($0 < \delta < 1$)) maximizes the density of available vacant states (more than 0.90 per int-Au), crucial for electron storage and photocatalytic activity. This oxidation-state balance is not only size-dependent, but is also strongly influenced by interfacial environments, such as exposed TiO_2 crystal facet and oxygen coordination. On the $\text{TiO}_2(001)$ surface, the Au cluster attains an optimal balance between metallic Au^0 and interfacial $\text{Au}^{\delta+}$ ($0 < \delta < 1$) species to maximize the electron storage capacity.

Overall, this study not only provides comprehensive structure–function correlations for Au/ TiO_2 catalysts but also establishes a methodological framework for realistic supported metal nanoparticle modeling. By bridging

the gap between small supported cluster models and experimental catalysts, our results on nanosize particles (~1.5 nm) demonstrate that explicit treatment of support reconstruction and oxygen incorporation is crucial for capturing the active interface chemistry, thereby offering guidelines for the rational design of facet-engineered and oxygen-modulated metal–oxide catalysts.

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Author Contributions

PS conceptualized and supervised the project. QL performed the calculations. YL and DC helped in the training of neural network potential. QL and PS wrote the paper.

Supplemental Information

Supporting Information. Supplementary methods; TiO₂ surface model; thermodynamics of Au/TiO₂ interface; Au/TiO₂ structural evolution with the introduction of O atoms; electronic structure.

Training dataset for Au–Ti–O G-NN potential is publicly available on Zenodo.

Preliminary URL (will be updated upon publication):

https://zenodo.org/records/16286683?preview=1&token=eyJhbGciOiJIUzUxMiJ9.eyJpZCI6ImU0NjI0ZjM0LWY3MmQtNGY4OC1iOTU5LWM0ZTgyODQxMDQ4OCIsImRhGEiOnt9LCJyYW5kb20iOiI2NDZzNTUwYzUzYjFiNTZlNDlkN2YzMTBhZTQzMTA1NyJ9.WYXEFaVdHYkzfMbsF2qU6sISXUNi9YNDqUxNBLZSoeW_qI8ER3c-oIk1Z13mDZPLw4OMbBEi4BBWPtarYQrEPA

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Notes

The authors declare no competing financial interest.

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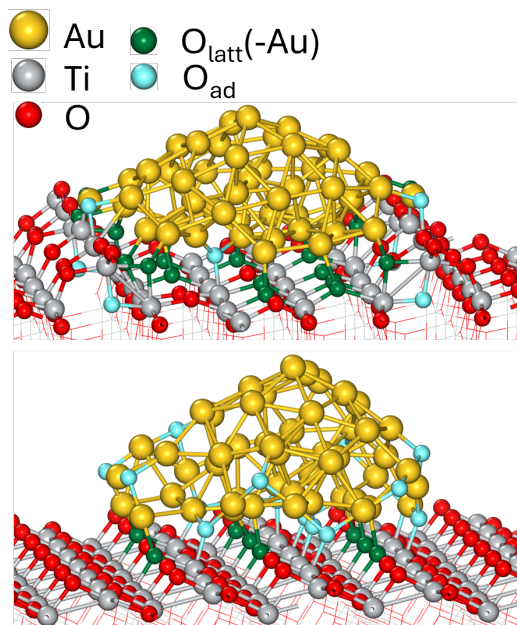
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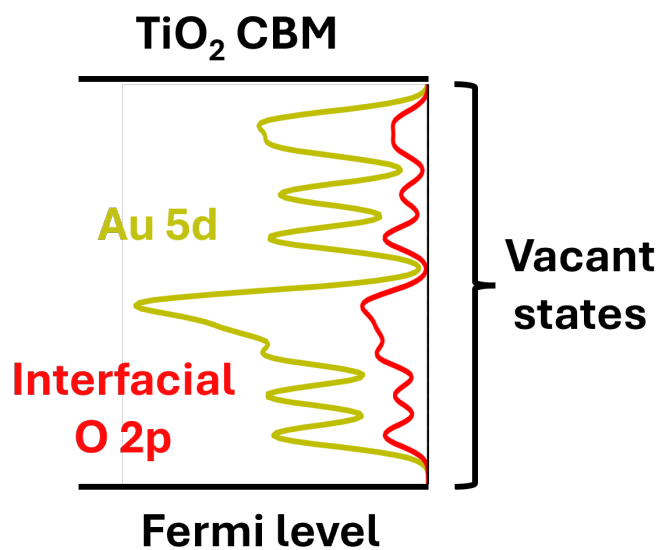
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Au/TiO₂ interface



Electron storage capacity

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