DFT Modeling of CO₂ Adsorption and HCOO⁺ Group Conversion in Anatase Au-TiO₂-Based Photocatalysis

Feitong Wu, Yanping Du, Sijia Lv, Changying Zhao,* and Xiang Yang

ABSTRACT: Due to the merits of carbon circulation and hydrocarbon production, solar-assisted photocatalysis has been regarded as an ideal option for securing a sustainable future of energy and environment. In the photocatalytic carbon cycle process, surface reactions including the adsorption of CO₂ and the conversion of CO₂ into CH₄, CH₃OH, etc. are crucial to be examined ascribed to their significant influence on the performance of the photocatalysis. Because the conversion reaction starts from the formation of HCOO⁺, the density functional theory (DFT) model was established in this study to investigate the micro-mechanism of CO₂ adsorption and the conversion of CO₂ to HCOO⁺ group in the anatase Au-TiO₂ photocatalytic system. The CO₂ adsorption bonding in six configurations was simulated, on which basis the effects of the proportion of water molecules and the lattice temperature increase due to the local surface plasmon resonance (LSPR) on the photocatalytic CO₂ adsorption and conversion were specifically analyzed. The results show that the experimental conditions that water molecules are released before CO₂ are favorable for the formation of the adsorption configuration in which HCOO⁺ tends to be produced without the need of reaction activation energy. This is reasonable since the intermediate C atoms do not participate in bonding under these conditions. Moreover, Au clusters have an insignificant influence on the adsorption behaviors of CO₂ including the adsorption sites and configurations on TiO₂ surfaces. As a result, the reaction rate is reduced due to the temperature increase caused by the LSPR effect. Nevertheless, the reaction maintains a very high rate. Interestingly, configurations that require activation energy are also possible to be resulted, which exerts a positive influence of temperature on the conversion rate of CO₂. It is found that the rate of the reaction can be improved by approximately 1–10 times with a temperature rise of 50 K above the ambient.

1. INTRODUCTION

In recent years, inspired by the carbon sequestration by the photosynthesis of green plants, artificial photosynthesis, which utilizes solar energy based on photocatalysts to enable the conversion of CO₂ into methanol, methane, and other hydrocarbon fuels, has become a research hotspot in the field of frontier science and technology.¹⁻⁴ On the one hand, the increasingly severe environmental problems caused by the greenhouse effect can be partly resolved using the photocatalytic technology.⁵⁻⁶ On the other hand, energy crisis and carbon reduction issues can be effectively alleviated due to the value-added hydrocarbon fuels through catalytic hydrogenation.⁷⁻⁸ Therefore, the emerging photocatalytic technology is of significance to achieve a clean and sustainable future, which fulfills the goal of carbon neutrality.⁹

In the process of photocatalytic carbon cycle, surface reaction is an important factor to be considered for the evaluation of efficiency. However, the reaction is based on the adsorption of CO₂ molecules on the catalyst surface.¹⁰,¹¹ With no adsorption of molecules, the catalytic reaction cannot be activated. Therefore, it is crucial to study the adsorption behaviors of CO₂ on the surface of the photocatalyst.

In anatase TiO₂, the (101) surface is the most stable and the most exposed surface. Comparatively, the anatase (001) surface has the advantage of higher catalytic activity despite relatively weaker features in stability and exposure area. Consequently, the anatase (001) surface has been widely involved in photocatalytic studies.¹² For example, Vittadini et al.¹³ investigated the dissociation behavior of molecules on (001) surfaces using the density functional theory (DFT). It was reported that the (001) surfaces were ideal sites for water to be dissociated. In addition, Ye et al.¹⁴ successfully prepared...
TiO$_2$(001), (101), (010) surfaces and studied the catalytic reduction of CO$_2$ to CH$_4$ when the exposure ratio of these three surfaces reached 90%. According to the fluorescence spectra, it was speculated that the electron-hole separation ability of the (001) surfaces was stronger than the other two crystal faces.

In the specific adsorption process, CO$_2$ molecules are first adsorbed on the (001) surface to absorb photogenerated electrons for the formation of HCOO$^-$. As the first step of the conversion, it is necessary to be examined as it is the basis of the subsequent reactions that convert the intermediates into hydrocarbon fuels such as CO, CH$_4$, CH$_3$OH, and HCOOH, affecting the whole reaction rate. It is worth mentioning that a series of subsequent reactions occur with the participation of water, which is oxidized by photogenerated holes to produce O$_2$. Apparently, there is certain competition between the water reduction and the CO$_2$ reduction in this step,$^{15}$ which is a unique step of photocatalytic reduction of CO$_2$ compared with others. Moreover, input energy is required to activate the reaction since the structure of CO$_2$ is highly stable and inert. As reported, the first-step reaction can only be realized at the potential of $-1.05$ eV, which is difficult to happen spontaneously without the addition of energy to overcome the reaction barrier in the uphill process. Nevertheless, CO$_2$ tends to be activated as a strong electron acceptor under the condition that hot electrons are promptly provided.

As a feasible approach, the local surface plasmon resonance (LSPR) effect can be utilized to generate hot electrons for the activation of CO$_2$. This is because significant surface heating by LSPR enables the molecules to overcome the high potential barriers in photocatalytic reactions.$^{16}$ The LSPR effect can be formed by loading Au, Ag, and other particles on TiO$_2$. With the combined effect of LSPR and the thermal confinement in the nano volume, the lattice temperature can be augmented in a few picoseconds as a result of the coupling of hot electrons and metal lattice phonons.$^{17,18}$ Jain et al.$^{19}$ studied the effect of femtosecond laser heating on gold nanoparticles attached to DNA ligands via thiol groups. The results showed that a Au–S bond could be destroyed, which was proven by the SPR peak shift of the Au NP.

In this study, the adsorption of CO$_2$ on a Au-TiO$_2$ porous catalyst was considered based on a newly established model based on the density functional theory (DFT) for the LSPR-supported photocatalysis. The micromechanism of CO$_2$ adsorption bonding in six configurations was studied. In addition, the effects of the proportion of water molecules and lattice temperature on CO$_2$ adsorption and conversion in the anatase Au-TiO$_2$ photocatalytic system were specified.

### 2. DFT MODELING FOR CO$_2$ ADSORPTION AND CONVERSION

The first-principles method based on DFT was used in the simulation. Since the periodic solid system on the surface of TiO$_2$ was considered, the periodic boundary conditions and the plane-wave basis set were applied. In the specific calculation, Vienna Ab initio Simulation Package (VASP) and the generalized gradient approximation (GGA) were adopted to describe the system. Moreover, the exchange-correlation interaction of the system was described by PBE functional.$^{20}$ For the description of the electron in the nucleus of the system, the pseudopotential method and PAW were used to approximate the inner electrons and check the role of valence electrons. The expansion of the wave function was controlled by the plane-wave base set, the size and energy of which were truncated. For structural optimization, the truncation energy of the plane-wave basis set was $400$ eV.$^{21}$ A plane-wave base set with truncation energy as twice that of the optimized structure was used to perform high-precision electronic step self-consistent calculation. The conditions for the end of structural optimization were that the force of all nuclei was less than $0.01$ eV/Å. The conditions for the end of the electron self-consistent cycle were that the total energy difference between the two steps was less than $1.0 \times 10^{-6}$ eV. The reciprocal space was sampled with $(2 \times 2 \times 1)$ $k$-point meshes. Periodic boundary conditions were set to simulate the surface of TiO$_2$ using supercells.$^{12}$ The (110) direction was defined as the $X$ direction, the (010) direction was defined as the $Y$ direction, and the (001) direction was defined as the $Z$ direction in the model. In the $X$ and $Y$ directions, the periodic expansion was assumed to be infinite, while in the $Z$ direction, a vacuum layer with a thickness of $15$ Å was inserted for the periodic expansion. During the structural optimization, other atoms in the bulk phase were fixed and the O–Ti–O atomic layer on the surface of (001) was released for the relaxation to the equilibrium position. Therefore, the slab model of the anatase TiO$_2$(001) surface was obtained, which was conducive to the description of plane waves.$^{22}$

First, the crystal plane model of anatase phase TiO$_2$(001) was established, as shown in Figure 1. The Ti atom in the bulk phase is 6-fold coordination, while the O atom is 3-fold coordination. Suspend bond exists when the TiO$_2$ crystal plane is peeled off from the solid-phase titanium dioxide; therefore, the unsaturated bond can be observed. The atoms on the TiO$_2$(001) crystal plane are divided into five-coordination Ti atom, two-coordination O atom, and three-coordination O atom, which are expressed as Ti$^{\ddagger}$, O$^{\ddagger}$, and O$_{3\ddagger}$, respectively. Herein, the stars represent unsaturated O and Ti atoms.

To further understand the reactive activity of TiO$_2$(001), the surface electrostatic potential distribution was plotted, as shown in Figure 2. It can be seen from the figure that the electrostatic potential of O$^{\ddagger}$ is larger than that of O$_{3\ddagger}$. This shows that the reactive activity of O$^{\ddagger}$ on the TiO$_2$(001) surface is comparatively higher. It has also been observed in the simulation that when the initial CO$_2$ molecule is placed...
above $O_{2c}^*$, the adsorption configuration of $C$ (CO$_2$) bonded to the surface $O_{2c}^*$ will be formed after the geometric optimization, as shown in Figure 3. The (b)−(d) configurations, with higher binding energies, belong to chemisorption. When the initial CO$_2$ molecule is placed above O$_3c$, the linear physisorption configuration (f) as shown in Figure 3 will be formed after the geometric optimization. The corresponding binding energy is calculated as 0.603 eV, which is far smaller than other chemical adsorption configurations. Therefore, when the reactant is adsorbed on the TiO$_2$(001) surface, the hydrogen atom in the hydroxyl group will first bond with $O_{2c}^*$.

The CO$_2$ adsorbed on the crystal face of anatase phase TiO$_2$(001) has different configurations. In this simulation, six models were established for the CO$_2$ adsorption, which determines the different adsorption energy of the system, as shown in Figure 3.$^{10,24,25}$ The first one is that the CO$_2$ molecule is linearly adsorbed ($\eta_1$) on the surface via the Oa atom (a). The second is that the CO$_2$ molecule is absorbed via the C atom to generate a monodentate carbonate ($\eta_1$) species (b). In the third, a bidentate carbonate ($\eta_2$) species is generated through the interaction of a CO$_2$ molecule with the surface via both the Oa and C atoms (c). The fourth is the generation of a bridged carbonate ($\mu_3-\eta_3$) geometry with the C atom of CO$_2$ pointing downward, forming a C−O bond; and two O atoms of CO$_2$ bind with two metal atoms to form a Ti−O bond with the Ti atom on the surface (d). In the fifth, a bridged configuration ($\mu_2-\eta_2$) with the C atom of CO$_2$ pointing upward and two O atoms of CO$_2$ binding with two metal atoms is formed (e). The presence of a Ti−O−Ti bond on the surface is contributed to the formation of the fourth or fifth model. The sixth is a linear physisorption that is not bonded (f). In the chemisorption configurations, they all have the common characteristic that C in CO$_2$ bonds with $O_{2c}^*$ in TiO$_2$, and O in CO$_2$ bonds with Ti in TiO$_2$. The dividing line between physisorption and chemisorption of CO$_2$ on the anatase TiO$_2$(001) surface is approximately 2.4 Å above Ti$_{3c}$ on the surface of TiO$_2$.

3. RESULTS AND DISCUSSION

3.1. Bond Length, Bond Angle, and Adsorption Energy.

$$E_{ad} = E_{total} - (E_{CO_2} + E_{TiO_2}) \ eV$$ (1)

The bond lengths, bond angles, and adsorption energies of CO$_2$ before and after adsorption in the six adsorption configurations are given in Tables 1 and 2. The adsorption energies are all negative (1), indicating that the adsorption process is exothermic and the adsorption structure is stable. In configurations (a)−(e), molecules form chemical bonds with the surface to reduce energy, leading to relatively stable chemisorption. In comparison, configuration (f) belongs to physisorption, with the adsorption energy significantly lower than that of the chemisorption.

![Figure 2](https://example.com/fig2.png)

**Figure 2.** Surface electrostatic potential distribution of TiO$_2$(001).

![Figure 3](https://example.com/fig3.png)

**Figure 3.** Adsorption configuration of CO$_2$ on TiO$_2$ surface: (a) linear chemisorption ($\eta_1$); (b) monodentate carbonate ($\eta_1$); (c) bidentate carbonate ($\eta_2$); (d) bridged carbonate ($\mu_3-\eta_3$); (e) bridged configuration ($\mu_2-\eta_2$); (f) linear physisorption.
In the bending adsorption configurations of (b), (c), (d), and (e), it is found that the bond angle after adsorption decreases significantly compared with that before adsorption, which is roughly between 135° and 140°. The bond length of CO₂ increases significantly and is approximately 1.26 Å after the adsorption process. In the linear physisorption configuration F, the bond length barely changes after the adsorption.

In contrast to the linear chemisorption, the bond angle is between the linear adsorption configuration and the curved configuration, which is slightly curved compared with the completely linear adsorption. This indicates that the chemical bonding on the surface of CO₂ and TiO₂ causes the redistribution of CO₂ charge. It breaks the original stable high symmetry of CO₂, which causes the electron cloud arrangement to converge to one side, thus causing slight local deformation on the surface of TiO₂.

### 3.2. Bonding Mechanism Analysis

CO₂ forms two stable π₂ delocalized bonds. Each π bond has two π electrons located on the lower bonding delocalized π orbital π(2pₓ)₁ or π(2pᵧ)₁, and the other pair of π electrons are located on the higher nonbonding molecular π orbital π(2pₓ)² or π(2pᵧ)², i.e., half-full, which shows that it has a certain electron giving ability and a certain electron receiving ability. The first ionization energy (13.79 eV) of CO₂ is significantly larger than that of the isoelectronic configuration of COS, CS₂, and N₂O; therefore, it is relatively difficult for CO₂ to give electrons. However, CO₂ is more receptive to electrons because of its lower half-full orbital (2π) and higher electron affinity (38 eV). The bond delocalization π orbitals are composed of two 2p orbitals provided by two O atoms.

After the adsorption, the internal bond length of CO₂ changes from 1.18 to 1.26 Å, and the covalency of the internal bond is weakened and the ionicity is enhanced. Figure 4 shows the sp hybrid orbital (σ orbital) and 1π orbital (highest energy occupied molecular orbital, HOMO) of CO₂ before adsorption and the 2π* orbital (lowest energy unoccupied molecular orbital, LUMO) peak at the Fermi level. After the adsorption, hybridization occurs between the Ti-d and O-p orbitals, indicating that the bonding happens between the Ti-d and O-p orbitals. However, the 2π* orbital shifts to the left due to the gain of electrons because Ti atoms give the d orbital electrons back to the 2π* antibonding orbital of CO₂ (Figure 5), which strengthens the degree of wave function offset between the CO₂ antibonding orbital and the bonding orbital. Con-

| adsorption configurations | CO₂ bond angle after adsorption (deg) | CO₂ bond length after adsorption (Å) | adsorption energy E_ad (eV) |
|---------------------------|--------------------------------------|------------------------------------|-----------------------------|
| (a) linear chemical adsorption (η₁) | 170.344 | 1.259, 1.297 | −3.75 |
| (b) monodentate carbonate (η₁) | 136.808 | 1.266, 1.266 | −4.61 |
| (c) bidentate carbonate (η₂) | 136.026 | 1.225, 1.281 | −4.36 |
| (d) bridged carbonate (μ₃−η₃) | 139.722 | 1.267, 1.267 | −5.57 |
| (e) bridged carbonate (μ₂−η₂) | 140.214 | 1.267, 1.267 | −4.01 |
| (f) linear physisorption | 179.226 | 1.179, 1.181 | −0.60 |

Figure 4. Partial density of states of CO₂ before and after adsorption.

Figure 5. Outer electron orbital cloud (d orbital) of Ti atoms.
sequently, the internal bonding of CO₂ is weakened and the internal bond length of CO₂ becomes longer.

As the surface of titanium dioxide is irradiated by light, electron–hole pairs are generated. The electrons and holes migrate to different positions on the surface of TiO₂. and REDOX reactions occur with the substances adsorbed on the surface of TiO₂. When an electron is transferred to the lowest unoccupied molecular orbital (LUMO) of CO₂, CO₂ is reduced to CO₂⁻ species. At this point, the bond angle of CO₂ decreases from 180° due to the repulsion between the two unshared electron pairs on the oxygen atom and the unshared electron pairs on the carbon atom. For example, the bond angle of the bent configuration (b) (e) mentioned above is approximately 135°–140°. Before adsorption, the energy gap between HOMO (highest molecular vacant orbital) and LUMO of CO₂ is as large as 13.7 eV, and the reduction potential of CO₂ molecule is a negative value of 0.6 ± 0.2 eV. Therefore, the chemical properties of CO₂ are relatively stable. As electrons are transferred to the LUMO, the gap between HOMO and LUMO decreases, and the excitation of electrons from HOMO to LUMO becomes easier. Consequently, the reaction energy barrier is reduced, and the reactivity is improved. Therefore, the CO₂ reduction adsorbed on the surface of the photocatalyst is extremely important. As multiple electrons migrate from the interior of the photocatalyst to the surface, the electrons and the corresponding number of protons are possible to participate in the reaction. For example, the formation of CH₄ requires eight electrons and eight protons. Therefore, the process of photocatalytic CO₂ reduction to generate organic compound fuel is bound to involve a multicomponent reaction. It is speculated that the regulation of thermochemical reduction potential exerts a significant effect on the generation of hydrocarbon fuels. This can be achieved by the selection of photocatalyst preparation and variations of reaction conditions. Typically, there are two common CH₄ formation pathways (i) CO₂ → HCOO⁻ → HCHO → CH₃OH → CH₃ and (ii) CO₂ → CO → C° → CH₂ → CH₄ However, it is worth mentioning that the reaction could be multipath due to the combined influence of multiple factors as mentioned above. For this reason, the first step of CO₂ transformation to the HCOO⁻ group in the first reaction path was simulated using the established model.

3.3. Influence of the Ratio of Water Molecules. It can be seen from Figure 6 that the HCOO⁻ group is obtained by connecting the H atom to the C atom. The linear CO₂ molecule is extremely stable and contains two C=O double bonds. The bond energy of the C=O double bond is 750 kJ/mol. The reduction of CO₂ starts from the formation of HCOO⁻. However, this process can only be realized at the potential of −1.05 V, which is difficult for many semiconductors to be fulfilled. Therefore, the first-step reaction is the main factor limiting the reaction rate.

First, the wettability needs to be introduced to the surface of TiO₂. In previous studies on the molecular adsorption of water, the oxygen atom of the water molecule binds to a Ti₅c atom, while in dissociative adsorption, there is an additional proton transferring from the chemisorbed water molecule to a bridging surface O₂c atom in the adjacent row. This type of dissociative adsorption can lead to the cleavage of Ti₅c−O₂c bonds on anatase (001), by the formation of Ti−OH (H₂O) bonds and O (TiO₂)−H (H₂O) bonds, as shown in Figure 7. Here, H atoms on the surface O₂c and OH groups on the surface Ti₅c are directly connected.

Then, different adsorption configurations were introduced to optimize the adsorption structure. As a consequence, the configurations of CO₂ and H₂O molecules were obtained. The effect of the ratio of CO₂ and water molecules on adsorption was studied by changing the ratio of CO₂ and water molecules (3:1, 2:1, 1:1, 1:2, 1:3).

In the adsorption of water, there are four basic conclusions as follows: first, H of water will form a hydrogen bond with O of TiO₂, thus occupying this adsorption site, increasing the difficulty of bonding between C (CO₂) and O (TiO₂); second, H of water will form a hydrogen bond with O of CO₂, thus increasing the difficulty of bonding O (CO₂) with Ti; third, O of hydroxyl will bind to the Ti on the surface, reducing the configuration of Ti bonding with CO₂; fourth, O of hydroxyl will combine with C (CO₂) to form −OOCOH, thus reducing the adsorption configuration of C (CO₂) to participate in bonding.

The effect of the H atom implies that the bridge carbonate adsorption configuration (d) of CO₂ on the dry surface may be transformed into bidentate carbonate η2 (c) and monodentate carbonate η1 (b) in the presence of water molecules. Part of the effect of increasing the proportion of water molecules is that it increases the probability that water will form hydrogen bonds with O in CO₂. The premise of this discussion is that CO₂ first approaches the O₂c point on the surface of TiO₂, which may correspond to the actual conditions that CO₂ is first released prior to that of water. However, under the condition
that CO₂ and water also compete for Ti adsorption sites, the occurrence probability of adsorption configurations without C bonding with TiO₂ surface may increase, including linear chemisorption η 1 (a), bridged carbonate μ2−η 2 (e), linear physisorption (f), etc. In the reaction path of CO₂ to CH₄, the first step involves the bonding of C; therefore, the exposed adsorption configuration of C (i.e., the reaction conditions under which CO₂ and water are released simultaneously or water is released before CO₂) may be favorable for this subreaction.

However, it should be noted that hydrogen bonds formed by H atoms are weaker than those formed by C(CO₂) and Ti and O(−OH), so the influence of hydroxyl groups on CO₂ adsorption may need to be considered. Simulation results show that when C(CO₂) does not bond with TiO₂ surface and O(−OH) does not bond with Ti, C(CO₂) will rapidly combine with O(−OH) to form a strong bond of −OOCOH. Under the condition that C(CO₂) bonds with TiO₂ surface and O(−OH) does not bond with Ti, C(CO₂) will break away from the existing bond and combine with O(−OH) alternatively. Therefore, it is speculated that simultaneous release of CO₂ and water has a negative influence on the conversion of CO₂ to HCOO* group.

3.4. Effect of Au on CO₂ Adsorption. The structure of Au-TiO₂ with the LSPR effect is different from that of Au-TiO₂ with doping modification. For the former, gold particles exist in the form of clusters, which are deposited on the surface of TiO₂ with a size in the range of 1−10 nm. For the latter, Au is doped in the lattice of TiO₂ in the form of metal ions.

In the study, gold nanoclusters of 5 nm are used to be adsorbed on the surface of TiO₂, occupying approximately 800 active adsorption sites of O₅c, O*₅c, and Ti*₅c, respectively. In the simulation, the influence of Au deposition (i.e., shape and size of Au clusters) on the preferred adsorption sites of CO₂ has been extensively investigated. This can be studied by featuring the adsorption behaviors of gold clusters in a small volume. Figure 8 presents the schematics of Au clusters and the simulated adsorption preference on the TiO₂ surface. As seen from the figure, the TiO₂ surface and Au clusters with lengths of 10 and 6 Å, respectively, were intercepted in the simulation to examine the adsorption behaviors as mentioned above. As adsorption sites on the TiO₂ surface can be typically recognized as the upper space of O₅c, O*₅c, and Ti*₅c, respectively, the proportions of different types of adsorption sites are analyzed in the simulation. Specifically, the ratios of O₅c,O*₅c,Ti*₅c of 2:2:1, 1:2:2, and 1:3:2 are considered in the study.

Based on the simulation, the adsorption of Au clusters is regarded as chemisorbed due to the presence of electrons to the TiO₂ surface. As a result, the catalytic performance in the photocatalytic reaction is promoted under the LSPR effect of Au clusters. This can be verified by the observed coexistence of the second LUMO, which indicates the transfer of thermal electrons evidenced by the strong coupling between Ti 3d orbital and Au sp orbital. Meanwhile, it is found that adsorption configurations as shown in Figure 8D–F change insignificantly after the simulation. This indicates that the adsorption of Au clusters has no preference on TiO₂ surfaces. Consequently, the adsorption sites of CO₂ on TiO₂ surfaces are reduced with no preference.

In an attempt to observe whether Au clusters would affect the adsorption configurations of CO₂, first, Au clusters as shown in Figure 8C are added to the TiO₂ surfaces adjacent to CO₂ with a distance of 1−2 Ti−O bond lengths. Subsequently, the adsorption behaviors of CO₂ with six configurations are specifically analyzed. In terms of the simulation results, Au clusters have an insignificant effect on the adsorption behaviors of CO₂ because of the no variation of the spatial positions of atoms in the CO₂ molecules.

The simulation results show that Au clusters have an insignificant influence on the adsorption behaviors of CO₂ including the adsorption sites and configurations on TiO₂ surfaces. These results are consistent with the literature. For example, according to the TPD analysis by Zeng et al.,¹ thirty most CO₂ is adsorbed on TiO₂ of the Au-TiO₂ photocatalyst. Moreover, in terms of the study by Hussain et al.,¹³ Au has weak interactions with CO₂ and H₂O in the catalytic system.

3.5. Transition-State Search and the Effect of Temperature. In the theory of reaction kinetics, the energy barrier of the catalytic reaction is an index to describe the degree of difficulty of chemical reactions. Therefore, it is significant to search for transition states and calculate the
reaction energy barrier when studying the conversion between CO₂ adsorption configurations and the reaction path of CO₂ to the HCOO group. Transition-state structure refers to the highest energy point on the reaction path on the potential energy surface. It connects the structures of the reactants and products (including intermediates in the case of multistep reactions) through a minimum energy path (MEP). This is beneficial to identify the adsorption configurations favorable for the catalytic reaction, providing a dimensional assessment for the selection of experimental conditions. In this step, complete LST/QST method was adopted to provide the structures of reactants (CO₂ and H atoms were adsorbed on the surface of TiO₂, respectively) and products (HCOO groups were adsorbed on the surface of TiO₂) under different adsorption configurations, and the parameters related to the structure optimization of the transition state were consistent with the adsorption structure optimization. The initial adsorption sites of the H atom were all approximately one Ti–O bond distance from the middle C atom after the CO₂ adsorption. To calculate the reaction barrier as accurately as possible, the number of interpolations of the transition states was augmented from the least to the most until the change in the reaction barrier was less than 0.01 eV. It is noted that the barrier is evaluated by the free energy of the transition-state structure and the free energy of the reactant structure.

Figure 9 shows the transition-state search curve of the reactant structure changing into the product structure under six adsorption configurations. The data of reaction energy and reaction barrier are shown in detail in Table 3. It can be seen that the reaction energies of all of the adsorption configurations are negative, which indicates that the reaction is exothermic. Among them, the reaction energies of most adsorption configurations are between −0.03 and −0.045 Ha, while the reaction energies of (e) and (f) configurations are larger, which are −0.0758 and −0.0904 Ha, respectively. It is inferred that the structure of the product is more stable than that of the reactants. The reaction barriers of (b)–(d) configurations are all positive, that is, the transition structure of the reactants is the most unstable at a certain moment during the transition to the product structure. Without energy input, the molecule tends to maintain the original reactant structure and the energy across this reaction barrier is provided by photoexcited TiO₂ electrons and the LSPR effect of Au. The energies of (a), (e), and (f) configurations decrease throughout the process of the transformation of the reactant structure to the product, which indicates that there is no transition state because the energy of the transition state is lower than that of the reactant. To ensure the situation, for the first step, the configurations are maintained the same transition-state structures. The results show that the energies of configurations (a), (e), and (f) from reactants to products still tend to decrease with no transition points in the middle. For the second step, the reactant and product structures of (a), (e), and (f), the calculation level, and the upper limit of small step length are changed for repetitive simulations. It is found that no transition state appears and the results are not affected by the above conditions. Therefore, it is concluded that for configurations (a), (e), and (f), there are no transition states. It is speculated that the structure of the reactant in configurations (a), (e), and (f) is more unstable and has a tendency to spontaneously transit to the product structure. It is noted that for the adsorption configurations of (a), (e), and (f), the C in the middle of CO₂ does not bond with TiO₂, therefore, it does not need to undergo the process of bond breaking and rebonding of the middle C atom when it is transformed into the product structure bonded by the middle C and H₂, which may be the reason for the avoidance of the reaction barrier.

The frequency analysis of the change of structures of the reactants and products to the first-step products in photo-

### Table 3. Energy States of Different Adsorption Configurations in Transition

| configurations | ΔE (Ha, reaction, Eᵣᵣᵣ – Eᵣᵣᵣ) | ΔEₖ (Ha, barrier, Eᵣᵣᵣ – Eᵣᵣᵣ) |
|----------------|-------------------------------|-------------------------------|
| a              | −0.0365                       | 0.0134                        |
| b              | −0.0453                       | 0.0157                        |
| c              | −0.0398                       | 0.0197                        |
| d              | −0.0410                       |                                |
| e              | −0.0758                       |                                |
| f              | −0.0904                       |                                |
catalysis was conducted for the six adsorption configurations. This is to obtain the relationship between the Gibbs free energy, a thermodynamic parameter, and the temperature (0−500 K). Equations 2 and 3 were used to calculate the Gibbs free energy change of the temperature-corrected reaction

\[ E_{\text{corr}}(T) = E_{\text{total}} + G_{\text{total}}(T) \]  

\[ \Delta G(\text{reaction}, T) = E_{\text{corr}}(\text{product}, T) - E_{\text{corr}}(\text{reactant}, T) \]

where \( G_{\text{total}}(T) \) is the Gibbs free energy difference corrected by temperature \( T \) for each structure, including the zero-point vibrational energy (ZPVE); \( E_{\text{total}} \) is the total energy of each structure, obtained from the frequency calculation output document; \( E_{\text{corr}}(T) \) denotes the Gibbs free energy of each structure under specific temperatures; and \( \Delta G(\text{reaction}, T) \) represents the change of Gibbs free energy in the transformation to the products in the first step of photocatalysis at various temperatures for the six adsorption configurations, as shown in Figure 10.

As can be seen from the transition-state search chart (Table 3), the reaction in which \( \text{CO}_2 \) is transformed into \( \text{HCOO}^* \) group is exothermic. It is shown from the chart that the Gibbs free energy change of the reaction is all negative and the reaction tends to be spontaneous. However, except for configurations (a), (e), and (f), all of the other reactions require certain reaction activation energy. Due to the consumption of \( \text{CO}_2 \) gas, this reaction is a reaction of entropy reduction. Therefore, with the increase of temperature, the molecular motion is strengthened and the thermal stability difference between \( \text{CO}_2 \) and \( \text{HCOO}^* \) group becomes smaller. This results in a positive slope in the curve of Figure 10, indicating that the absolute value of Gibbs free energy change of the reaction becomes smaller with the increase of temperature.

For a long time, there are three hypotheses for the explanation of the enhancement of catalytic activity by surface plasmas, which are temperature rise, molecular photoexcitation, and hot electron injection.33 Plasma resonance energy causes the local lattice temperature to increase sharply in a few picoseconds.35 In this study, the tunneling effect and variational transition state theory (VTST) are not considered in the simulation.36 Instead, it is assumed that the concentrations of \( \text{CO}_2 \) molecules and \( \text{H} \) atoms of the reactants are maintained in the process and are both in the gas phase. The classical transition-state theory was used to investigate the influence of temperature on the degree of difficulty of the reaction. Based on the assumptions, the half-life of the reaction \( T_{1/2} \) (the time required to reduce the reactant concentration to half of the initial concentration) was calculated according to the TST formula, as given in eqs 4−6

\[ k = \sigma k_B T \left( \frac{k_B T}{P_0} \right)^\Delta n e^{-\Delta G^0/(k_B T)} \]  

\[ \Delta G_0^0(T) = G_{TS}(T) - G_{\text{reactant}}(T) \]  

\[ T_{1/2} = \frac{1}{[A_0]k} \]

where \( k \) is the reaction rate constant in \( \text{s}^{-1}(\text{molecules/cm}^3)^{-1} \); \( \sigma \) is the degeneracy of reaction path, which is 1; \( k_B \) is the Boltzmann constant, which is \( 1.3806503 \times 10^{-23} \) J/K; \( T \) is the temperature in K; \( h \) is Planck’s constant, which is \( 6.6260696 \times 10^{-34} \) J·s; \( P_0 \) is the standard atmospheric pressure, 1 bar; \( \Delta n \) is related to the number of reactant molecules N, which is equal to \( N - 1 \); \( \Delta G^0^0(T) \) denotes the temperature-adjusted free energy difference between the transition structure \( G_{TS}(T) \) and the reactants at standard atmospheric pressure \( G_{\text{reactant}}(T) \) in kJ/mol; \( T_{1/2} \) represents the half-life, which is the time required to reduce the concentration of the reactants to half the initial
concentration, in s; and $[A_0]$ is the initial concentration of the reactants, which is assumed to be 1 M in the calculation.

The variation of the reaction half-life with temperature is shown in Table 4 and Figure 11. It can be seen that the curves are divided into two categories, one is configurations (b)–(d), which are the adsorption configurations requiring reaction activation energy, and the other is configurations (a), (e), and (f), which represent the adsorption configurations without reaction activation energy. The reaction half-life of the former is very large at low temperatures (0 K to approximately 100 K), which implies the impossibility of the reaction. However, as the temperature gradually increases, it provides energy to overcome the reaction barrier, and the half-life decreases rapidly. At the room temperature of 298.15 K, the half-life can reach the order of nanoseconds to picoseconds. As the temperature continues to increase, the reaction rate accelerates continuously, but the change of the time order is not dramatic. The reaction rate of the latter is extremely fast at low temperatures. With the increase of temperature in the exothermic reaction, both the positive reaction and the reverse reaction are accelerated. However, the reverse reaction is more intense, leading to a slower positive reaction rate and longer half-life. Compared with (b)–(d) configurations, their half-lives still have a prominent advantage of tens of orders of magnitude.

The effect of the temperature rise caused by plasma resonance is discussed based on room temperature. It is found that the reaction rate of (a), (e), and (f) configurations is insignificantly reduced. However, the reaction still proceeds at a high rate within picoseconds. Interestingly, the temperature rise is beneficial for (b)–(d) configurations, which need to overcome the reaction barrier. Above the room temperature, the half-life decreases by $0\sim 1$ order of magnitude with every 50 K increase of temperature, resulting in an increase of the reaction rate by $1\sim 10$ times. It is worth mentioning that the above analysis is in the premise that the influence of the TiO$_2$ catalyst which

| temperature (K) | a       | b       | c       | d       | e       | f       |
|----------------|---------|---------|---------|---------|---------|---------|
| 50             | $7.103 \times 10^{-213}$ | $1.205 \times 10^4$ | $6.245 \times 10^{12}$ | $2.954 \times 10^{20}$ | $7.265 \times 10^{24}$ | $1.233 \times 10^{27}$ |
| 100            | $1.879 \times 10^{115}$ | $2.904 \times 10^6$ | $2.855 \times 10^5$ | $5.559 \times 10^3$ | $8.416 \times 10^5$ | $8.787 \times 10^4$ |
| 150            | $3.584 \times 10^{13}$ | $1.831 \times 10^9$ | $1.073 \times 10^6$ | $6.954 \times 10^4$ | $8.545 \times 10^9$ | $3.523 \times 10^8$ |
| 200            | $4.032 \times 10^{7}$ | $5.025 \times 10^{11}$ | $7.338 \times 10^6$ | $8.501 \times 10^4$ | $4.933 \times 10^{15}$ | $1.278 \times 10^{15}$ |
| 250            | $1.490 \times 10^7$ | $6.181 \times 10^{12}$ | $3.960 \times 10^6$ | $1.617 \times 10^8$ | $1.552 \times 10^{18}$ | $3.041 \times 10^{18}$ |
| 298.15         | $2.038 \times 10^{11}$ | $1.651 \times 10^{12}$ | $6.229 \times 10^{10}$ | $1.296 \times 10^9$ | $8.567 \times 10^{14}$ | $1.398 \times 10^{13}$ |
| 350            | $1.497 \times 10^{16}$ | $5.798 \times 10^{13}$ | $1.537 \times 10^{10}$ | $1.902 \times 10^8$ | $3.382 \times 10^{18}$ | $4.524 \times 10^{18}$ |
| 400            | $4.977 \times 10^{16}$ | $2.904 \times 10^{13}$ | $5.671 \times 10^{11}$ | $4.856 \times 10^{11}$ | $1.095 \times 10^{17}$ | $1.336 \times 10^{17}$ |
| 450            | $2.087 \times 10^{11}$ | $1.709 \times 10^{13}$ | $2.633 \times 10^{11}$ | $1.693 \times 10^{11}$ | $8.970 \times 10^{16}$ | $1.019 \times 10^{16}$ |
| 500            | $2.587 \times 10^{11}$ | $1.123 \times 10^{13}$ | $1.432 \times 10^{11}$ | $7.312 \times 10^{12}$ | $2.843 \times 10^{14}$ | $3.053 \times 10^{14}$ |

Figure 11. Half-life ($T_{1/2}$) of the reaction as a function of temperature.
provides the activation energy required for the reaction is not considered.

4. CONCLUDING REMARKS

In this study, we focus on the adsorption mechanism of CO2 on the anatase phase Au-TiO2(001) crystal plane and examine the behavior of the first step reaction for converting to the HCOO* group in the photocatalytic reduction of CO2 to the CH4 path. The influence of the water molecules ratio and the temperature rise due to LSPR are specifically discussed. Based on the model, it is concluded that the role of adsorption in CO2 reduction is to weaken the internal bonding of CO2 and activate CO2 molecules. Moreover, the way CO2 is converted to HCOO* group is that the middle C atom bonds with an H from H2O2 therefore, the adsorption configuration for which the middle C atom does not participate in the bonding is conducive to this step reaction. Due to the competitive adsorption sites, this corresponds to the experimental conditions that water molecules are released prior to CO2. Au clusters have an insignificant influence on the adsorption behaviors of CO2 including the adsorption sites and configurations on TiO2 surfaces. The conversion of CO2 to HCOO* group is an exothermic reaction, and the adsorption configurations in which the intermediate C atom does not participate in bonding do not require activation energy in the reaction. For these configurations that do not require activation energy, the reaction rate is reduced due to the temperature increase caused by the LSPR effect of Au. However, the reaction continues at a very high rate, which occurs within picosecond magnitude. However, the activation energy is indispensable in other adsorption configurations and can be provided by the catalytic action of TiO2 in the photocatalysis. Comparatively, the reaction rate for these configurations is approximatley 1–10 times improved with every 50 K increase of temperature above the ambient.

§

AUTHOR INFORMATION

Corresponding Authors
Yanping Du — China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai 201306, China; orcid.org/0000-0001-7393-6406; Email: yanping.du@sjtu.edu.cn
Changying Zhao — China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai 201306, China; Institute of Engineering Thermophysics, Shanghai Jiao Tong University, Shanghai 200240, China; orcid.org/0000-0003-0023-0378; Email: changying.zhao@sjtu.edu.cn

Authors
Feitong Wu — China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai 201306, China
Sijia Lv — China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai 201306, China
Xiang Yang — China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai 201306, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c06861

Author Contributions
$F.W. and Y.D. contributed equally to this work.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The research was financially supported by the National Natural Science Foundation of China (no. 52076139), Shanghai Pujiang Talent Program (19PJ1405100), and Shenlan Program at Shanghai Jiao Tong University (SL2020MS004).

■ REFERENCES

(1) Lee, S.; Yong, J. G.; Kyu, K. J.; Hyekoo, P. J. Solar-harvesting lead halide perovskite for artificial photosynthesis. J. Energy Chem. 2021, 62, 11–26.
(2) Liangjiao, T.; Qi, X.; Chang, Z.; Guancai, Z.; Zain, A. M.; Wenrong, W.; Renping, M.; Xinrui, J.; Beidou, G.; Ru, G. J. Nanoarray Structures for Artificial Photosynthesis. Small 2021, 17, No. 202006530.
(3) Zhang, Z.; Yi, G.; Li, P.; Zhang, X.; Fan, H.; et al. Engineering approach toward catalyst design for solar photocatalytic CO2 reduction: A critical review. Int. J. Energy Res. 2021, 45, 9895–9913.
(4) Hongxia, W.; Yanjie, W.; Linggu, G.; Xuehua, Z.; Ribeiro, C. Full spectrum photocatalytic reduction of CO2 catalyzed by photothermal effect. Chin. J. Catal. 2020, 41, 141–152.
(5) Andrés, G. G.; Niall, M. D.; Nilay, S. A. Carbon neutral chemical industry powered by the sun. Discov. Chem. Eng. 2021, 1, No. 2.
(6) Guangbo, C.; Geoffrey, W.; Run, Sj.; Jiaqing, Z.; Zhenhua, L.; Lizhu, W.; Chen-Ho, T.; Tierui, Z. From Solar Energy to Fuels: Recent Advances in Light-Driven C1 Chemistry. Angew. Chem. Int. Ed. 2019, 58, 17528–17551.
(7) Steven, B.; Audrey, B.-S.; Antoine, F.; Zhenpeng, C.; Christophe, C.-J.; Valérie, C.; Valérie, K. Plasmonic photocatalysis applied to solar fuels. Faraday Discuss. 2019, 214, 417–439.
(8) Ameta, R.; Panchal, S.; Ameta, N.; Ameta, S. C. Photocatalytic Reduction of Carbon Dioxide. In Materials Science Forum; Trans Tech Publications Ltd, 2013; Vol. 764.
(9) Liu, Q. Study on the Adsorption and Diffusion of Nitric Oxide and Nitrogen Atoms on TiO2 Photocatalyst; Wuhan University, 2017.
(10) Mino, L.; Spoto, G.; Ferrari, A. M. CO2 Capture by TiO2 Anatase Surfaces: A Combined DFT and FTIR Study. J. Phys. Chem. C 2014, 118, 25016–25026.
(11) Wen, M.; Kuwahara, Y.; Mori, K.; Yamashita, H. Enhancement of Catalytic Activity Over AuPd Nanoparticles Loaded Metal Organic Framework Under Visible Light Irradiation. Top. Catal. 2016, 59, 1765–1771.
(12) Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Cheng, H. M.; Lu, G. Q. Anatase TiO2 single crystals with a large percentage of reactive facets. Nature 2008, 453, 638–641.
(13) Vittadini, A.; Selloni, A.; Rottinger, F. P.; et al. Structure and Energetics of Water Adsorbed at TiO2 Anatase (101) and (001) Surfaces. Phys. Rev. Lett. 1998, 81, 2954–2957.
(14) Ye, L.; Jin, M.; Tianyou, P.; Ling, Z.; Youxiang, Z. Opposite photocatalytic activity orders of low-index facets of anatase TiO2 for liquid phase dye degradation and gaseous phase CO2 photoreduction. Phys. Chem. Chem. Phys. 2014, 16, 15675–15680.
(15) Xiaoxiao, Z. Photocatalytic Reduction of CO2 by BiOBr; Henan University, 2020.
(16) Fasciani, C.; Alejo, C. J. B.; Grenier, M.; Netto-Ferreira, J. C.; Sciano, J. C. High-Temperature Organic Reactions at Room-Temperature Using Plasmon Excitation: Decomposition of Dicumyl Peroxide. Org. Lett. 2011, 13, 204–207.
(17) Hartland, G. V. Optical studies of dynamics in noble metal nanostructures. Chem. Rev. 2011, 111, 3858–3887.
(18) Christopher, P.; Xin, H.; Linic, S. Visible-light-enhanced catalytic oxidation reactions on plasmonic silver nanostructures. Nat. Chem. 2011, 3, 467–472.
(19) Jain, P. K.; Qian, W.; El-Sayed, M. A. Ultrafast cooling of photoexcited electrons in gold nanoparticle-thiolated DNA conjugates involves the dissociation of the gold-thiol bond. J. Am. Chem. Soc. 2006, 128, 2426–2433.
(20) Zhou, J.; Liu, G.; Jiang, Qi; Zhao, W.; Ao, Z.; An, T. Density functional theory calculations on single atomic catalysis: Ti-decorated...
Ti3C2O2 monolayer (MXene) for HCHO oxidation. *Chin. J. Catal.* 2020, 41, 1633−1644.

(21) Sorescu, D. C.; Al-Saidi, W. A.; Jordan, K. D. CO2 adsorption on TiO2(101) anatase: a dispersion-corrected density functional theory study. *J. Chem. Phys* 2011, 135, No. 124701.

(22) Wanbayor, R.; Deak, P.; Frauenheim, T.; Ruangpornvisuti, V. First principles theoretical study of the hole-assisted conversion of CO to CO2 on the anatase TiO2(101) surface. *J. Chem. Phys.* 2011, 134, No. 104701.

(23) Mete, E.; Gülerseren, O.; Ellialtılıoglu, S. Modification of TiO2(001)surface electronic structure by Au impurity investigated with density functional theory. *Phys. Rev. B* 2009, 80, No. 035422.

(24) Sorescu, D. C.; Al-Saidi, W. A.; Jordan, K. D. CO2 adsorption on TiO2(101) anatase: a dispersion-corrected density functional theory study. *J. Chem. Phys.* 2011, 135, No. 124701.

(25) Yin, W. J.; Krack, M.; Wen, B.; Ma, S. Y.; Liu, L. M. CO2 Capture and Conversion on Rutile TiO2(110) in the Water Environment: Insight by First-Principles Calculations. *J. Phys. Chem. Lett.* 2015, 6, 2538−2545.

(26) Dhakshinamoorthy, A.; Navalon, S.; Corma, A.; Garcia, H. Photocatalytic CO2 reduction by TiO2 and related titanium containing solids. *Energy Environ. Sci.* 2012, 5, 9217−9233.

(27) Varilla, L. A. A.; Seriani, N.; Montoya, J. A. Molecular adsorption and dissociation of CO2 on TiO2 anatase (001) activated by oxygen vacancies. *J. Mol. Model.* 2019, 25, No. 231.

(28) Tsimel, M. A review and recent advances in solar-to-hydrogen energy conversion based on photocatalytic water splitting over doped-TiO2 nanoparticles. *Solar Energy* 2020, 211, 522−546.

(29) Xiang, Q.; Lv, K.; Jiaguo, Y. Pivotal role of fluorine in enhanced photocatalytic activity of anatase TiO2 nanosheets with dominant (001) facets for the photocatalytic degradation of acetone in air. *Appl. Catal., B* 2010, 96, 557−564.

(30) Zhu, D. D.; Liu, J. L.; Qiao, S. Z. Recent Advances in Inorganic Heterogeneous Electrocatalysts for Reduction of Carbon Dioxide. *Adv. Mater.* 2016, 28, 3423−3452.

(31) Raja, M.; Kim, S.-Y.; van Duin, A. C. T.; Fichthorn, K. A. ReaxFF Reactive Force Field Study of the Dissociation of Water on Titania Surfaces. *J. Phys. Chem. C* 2013, 117, 10558−10572.

(32) Zeng, S.; et al. Optical control of selectivity of high rate CO2 photoreduction via interband- or hot electron Z-scheme reaction pathways in Au-TiO2 plasmonic photonic crystal photocatalyst. *Appl. Catal., B* 2020, 267, No. 118644.

(33) Hussain, A.; Gracia, J.; Nieuwenhuys, B. E.; Niemantsverdriet, J. W. H. Explicit Roles of Au and TiO2 in a Bifunctional Au/TiO2 Catalyst for the Water-Gas Shift Reaction: A DFT Study. *ChemCatChem* 2013, 5, 2479−2488.

(34) Pipornpong, W.; Wanbayor, R.; Ruangpornvisuti, V. Adsorption CO2 on the perfect and oxygen vacancy defect surfaces of anatase TiO2 and its photocatalytic mechanism of conversion to CO. *Appl. Surf. Sci.* 2011, 257, 10322−10328.

(35) Yadav, R.; Amoli, V.; Singh, J.; Tripathi, M. K.; Bhanja, P.; Bhauumik, A.; Sinha, A. K. Plasmonic gold deposited on mesoporous TiSi1−O2 with isolated silica in lattice: An excellent photocatalyst for photocatalytic conversion of CO2 into methanol under visible light irradiation. *J. CO2 Util.* 2018, 27, 11−21.

(36) Yuan, W.; Zhang, D.; Ou, Y.; Fang, K.; Zhu, B.; Yang, H.; Hansen, T. W.; Wagner, J. B.; Zhang, Z.; Gao, Y.; Wang, Y. Direct In Situ TEM Visualization and Insight into the Facet-Dependent Sintering Behaviors of Gold on TiO2. *Angew. Chem., Int. Ed. Engl.* 2018, 57, 16827−16831.

(37) Tian Lu, T. Excel Spreadsheet for Calculating Reaction Rate Constants Based on Transition State Theory, 2021. http://sobereva.com/310.