**INTRODUCTION**

The concentration of carbon dioxide (CO$_2$) in the atmosphere, one of the major greenhouse gases, grew by more than 6% in the past decades, causing rapid climate change. Thus, the conversion of CO$_2$ is an urgent challenge, which attracts plenty of attention in research. Many efforts have been made to reduce this inert molecule to useful chemicals such as carbon monoxide, formic acid, and fuel molecules such as methane and methanol. The most common methods are electrocatalysis and photocatalysis, of which the latter is particularly attractive because it utilizes solar energy to achieve the zero-carbon emission reduction process. However, the energy efficiency of photocatalysis is very low (only 3.8% of that of electrolysis). In this vein, photoelectrochemical reduction is on the rise in this field, because it inherits the advantages of photocatalysis (the use of solar energy) and at the same time avoids the disadvantages such as low photogenerated electron–hole separation efficiency, reoxidation of the products, and the insufficient conduction band edge level.

Halmann reported a pioneering work on the photoelectrocatalytic reduction of CO$_2$ on an irradiated p-type semiconductor, GaP, in the presence of an applied bias potential. Barton et al. reached a nearly 100% faradaic efficiency of CO$_2$ photoelectrochemical reduction at p-GaP electrodes with homogeneous pyridinium ion catalysts. Recently, Qiu et al. achieved artificial photosynthesis by using TiO$_2$-passivated InP nanopillar photocathodes under illumination. Song et al. developed a highly selective and efficient photoelectrode by photolithographically plating a nanoporous Au film on Si electrode. CO, HCOOH, and CH$_3$OH are the main products of the photoelectroreduction in these experimental works.

On the theoretical side, many methods have been recently implemented to apply electrochemical potential in quantum chemical calculation under the periodic boundary conditions, including charging the slab and providing a compensating homogeneous background charge, explicit ions, the grand canonical potential kinetics, and the linear free energy relationship for the electrochemical potential with the computational hydrogen electrode (CHE) model, where some of them have been already applied on the semiconductor system. The solvent/electrolyte, which plays an important role in the electrochemical process, is most of the time treated implicitly. However, all applications of these methods involve the electrochemical CO$_2$ reduction reaction (CO$_2$RR) on a metallic cathode. Simulations have not yet addressed the (photo)electrocatalytic CO$_2$RR on semiconductors.
tor cathodes, and it is still unknown how the applied electrochemical potential and solvent/electrolyte affect the heterogeneous CO$_2$RR at such interfaces of semiconductors.

The cathode in a (photo)electrochemical cell can directly convert CO$_2$ through a series of multielectron hydrogenation processes:

\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2e^- &= \text{HCOOH} \\
\text{CO}_2 + 2\text{H}^+ + 2e^- &= \text{CO} + \text{H}_2\text{O} \\
\text{CO}_2 + 4\text{H}^+ + 4e^- &= \text{HCHO} + \text{H}_2\text{O} \\
\text{CO}_2 + 6\text{H}^+ + 6e^- &= \text{CH}_4\text{OH} + \text{H}_2\text{O} \\
\text{CO}_2 + 8\text{H}^+ + 8e^- &= \text{CH}_4 + 2\text{H}_2\text{O}
\end{align*}
\]

to generate useful species, or indirectly further hydrogenate the intermediates:

\[
\begin{align*}
\text{CO} + 2\text{H}^+ + 2e^- &= \text{HCHO} \\
\text{HCHO} + 2\text{H}^+ + 2e^- &= \text{CH}_4\text{OH} \\
\text{HCHO} + 4\text{H}^+ + 4e^- &= \text{CH}_4 + \text{H}_2\text{O}
\end{align*}
\]

while the oxygen evolution reaction should occur on the anode, giving rise to protons that can migrate to the cathode. The TiO$_2$ film is a common material that would be deposited on a metallic electrode in the electrochemical cell, or the semiconductor electrode in the photoelectrochemical cell, because of its stability against corrosion, high current efficiency, and low valence band edge to fulfill a current cycle. For instance, the InP photocathode gets significantly degraded after 0.5 h illumination under the photoelectrochemical condition, whereas the TiO$_2$-passivated one remains stable for at least 12 h. Therefore, the TiO$_2$ material in this circumstance plays an important role as a catalyst and a protector rather than a light harvester. Understanding the mechanism of (photo)electrocatalytic CO$_2$RR requires consideration of the TiO$_2$ surface is in the electrochemical conditions. Moreover, the overpotential is a key factor to understanding the (photo)electrocataly reaction as well, which was theoretically thought to be controlled by binding energies in each elementary step only. Recently, we elucidated a part of the mechanism of the photoreduction of CO$_2$ on the defective anatase TiO$_2$ (101) surface, on the basis of density functional theory (DFT) calculations. This study revealed the essential role of the oxygen vacancy in the CO$_2$RR process. In this work, we consider CO$_2$RR on defective anatase TiO$_2$ (101) under an electrochemical potential, to simulate the (photo)-electrocatalytic scenario and to elucidate the differences in the adsorption and reaction processes on the pristine and defective surfaces and at the vacuum/catalyst (V/C), solvent/catalyst (S/C), and electrolyte/catalyst (E/C) interfaces.

### COMPUTATIONAL DETAILS

Spin-polarized density functional theory (DFT) calculations corrected by on-site Coulomb interaction were performed with the Vienna Ab initio Simulation Package (VASP). The projected augmented-wave (PAW) and the Perdew, Burke, and Ernzerhof (PBE) generalized gradient approximant functionals were utilized throughout this study. A cutoff energy of 400 eV was set, and a 3.5 eV effective U value was applied to the 3d orbitals of Ti to better describe the electron localization at the oxygen vacancy. The 0.5 M KCl aqueous solution with the dielectric constant of 78.4 was treated implicitly, using the VASP sol code, in the S/C and E/C interface simulations. All of the transition state configurations were located via the climbing image nudged elastic band (CI-NEB) method. The Bader charge analysis was utilized to study the charge distributions.

The anatase TiO$_2$ (101) was modeled as a symmetric slab, built from a (3 × 1) supercell of an optimized anatase cell. It consisted of 30 atomic layers with the middle six layers fixed, as illustrated in Figure 1. In this model, the surface slab consisted of the surface area (the 1st, 3rd, 28th, and 30th atomic layers), the subsurface area (the 2nd, 4th–6th, 25th–27th, and 29th atomic layers), the transition area (the 7th–12th and 19th–24th atomic layers), and the bulk area (the 13th–18th atomic layers), of which the last two were called the inner layer area in this work. A 20 Å vacuum layer was placed between the slabs to avoid their interactions along the z-direction. The surface oxygen atoms in the center of the outermost oxygen layers on both sides of the slab were removed to simulate the defective surface. Reactant molecules were symmetrically put on both sides to counter the possible polarization of the dipole.

The applied electrochemical potential was simulated by the linearized Poisson–Boltzmann equation method as implemented in the VASP sol code. In this method, a certain net charge $q$ is introduced into the electrode slab, and the corresponding compensating background charge $q_{\text{bg}} = -q$ is added into the electrolyte, to keep the whole system charge-neutral. The absolute electrode potential, $\phi$, is obtained by subtracting the Fermi energy from the energy level of the electrolyte, and the result numerically equals the work function. Therefore, the applied electrochemical potential versus standard hydrogen electrode, $\phi_{\text{SHE}}$, is given by

\[
\phi_{\text{SHE}} = \phi - 4.44
\]

where 4.44 V is the recommended absolute potential of the H$^+/\text{H}$ redox pair in aqueous solutions. Because of the
existence of net charge, the total DFT energy should be grand canonically corrected as the electronic free energy, \(^{44}E^{\text{free}}\):

\[
E^{\text{free}} = E_{\text{DFT}}(q) + q\phi
\]

where \(E_{\text{DFT}}\) is the calculated total energy of the system with corresponding net charge. The extrapolating linear and quadratic fittings were applied for the relationships between \(q\) and \(\phi\) and \(E^{\text{free}}\) and \(\phi_{\text{SHE}}\), respectively, with both coefficients of determination being over 0.999.

From this model, we can retrieve the adsorption, reaction, and activation energies during the DFT calculations. The adsorption energy for each molecule, \(E_{\text{ads}}\), was calculated by

\[
E_{\text{ads}} = \frac{1}{2}(E^{\text{free}}_{\text{adsorbate@slab}} - 2E_{\text{adsorbate}} - E^{\text{free}}_{\text{slab}})
\]

where \(E^{\text{free}}_{\text{adsorbate@slab}}\) and \(E^{\text{free}}_{\text{slab}}\) stand for the calculated electronic free energies of the cathode slab with and without adsorbates, respectively, and \(E_{\text{adsorbate}}\) represents the calculated energy of the corresponding adsorbate.

The corresponding con...
the main reactant, is no longer adsorbed on either surface, despite the positive effect of the oxygen vacancy (Ov) sites on the adsorption, which is consistent with the early computational work on the TiO$_2$ cluster model. CO is bound to both surfaces with a rather small adsorption energy and thus remains the carbon source for the reduction reaction. Other carbon-based species, for example, carbonate, could be present and participate in the entire reduction process, which was not considered in this work. As for the products, the desorption becomes much easier from the S/C interface than from the V/C interface. At the pristine surface, the adsorption energies of CH$_2$O and CH$_3$OH are halved with the presence of the aqueous solvent, suggesting the direct desorption of these species in mild conditions. On the other hand, at the defective surface, these species appear to be trapped at the Ov site, with adsorption energies below $-0.63$ eV, despite the electronic passivation. Because of the strong adsorption of CH$_2$O, it should undergo further reduction. CH$_3$OH can bind to the surface endothermically by $0.19$ eV and be released without an energy barrier. CH$_4$, which has adsorption energies compatible with its release as a product, is hardly influenced by the solvent effect, as expected on the basis of its insignificant polarity.

The conversion between CO$_2$ and CO species at both V/C and S/C interfaces of the defective surface was calculated and illustrated in Figures 3 and S3. At the V/C interface, the main CH$_4$ products through the CHO*, CH$_2$O*, CH$_3$O*, or CH$_2$OH* intermediates, based on our previous investigation (see Figures 4a and S4). At the V/C interface (black line in Figure 4), the adsorbed CO successively binds protons at the carbon site in the first two hydrogenation steps, with enthalpy variations of $0.06$ and $-0.81$ eV, respectively. The first step producing the CH$_3$O* intermediate has a larger activation energy of 1.41 eV. The CH$_3$O* intermediate binds to the surface strongly, which has to combine with another proton at the carbon site with a barrier of 0.80 eV, to generate the CH$_4$O* intermediate, and release a considerable amount of energy (1.27 eV). There is an alternative feasible pathway where the oxygen site of the CH$_3$O* intermediate binds a proton to generate CH$_3$OH*, with a barrier higher by 0.19 eV, and reaction endothermicity of 0.33 eV. The presence of the solvent does not create a big difference in the reaction profile (the red and black pathways in Figure 4 nearly overlap). In fact, the maximum cumulative difference of these steps is only 0.08 eV.

Both CH$_3$O* and CH$_2$OH* intermediates can participate in the final hydrogenation step to generate the products, CH$_3$OH and CH$_4$, as illustrated in Figures 4 and S4. During the final hydrogenation process at the V/C interface, the CH$_3$O* intermediate preferentially exothermically binds a proton at the carbon site, forms CH$_3$OH*, and with its oxygen atom, and generates methane. The barrier for this step is as high as 1.47 eV, making it the rate-determining step. CH$_3$O* also can bind a proton at the oxygen site, forming the CH$_3$OH* intermediate, with a 0.77 eV lower barrier. However, the reaction energy for this alternative process is 0.69 eV, and the desorption energy for methanol is 1.21 eV, which makes the process thermodynamically forbidden. Similarly, despite an exothermic production of CH$_3$OH*, with a lower activation energy of 1.04 eV, the CH$_3$OH* intermediate finally results in CH$_4$, because of the strong adsorption of methanol. Thus, only methane is generated at the V/C interface of the defective surface. When this process happens at the S/C interface, the solvent effect slightly enhances the reactions. The enthalpies of all reaction steps decrease by more than 0.1 eV, and the corresponding barriers also have obvious downshifts. Because of the weak adsorption of methanol at the S/C interface, the pathway involving the CH$_3$OH* intermediate is the kinetically favorable one to generate methanol.

Overall, at the V/C interface, because of the strong adsorption of methanol, CH$_4$ is produced from CO$_2$ through the CO$_2$ + CO* → CHO* → CH$_2$O* → CH$_3$O* → CH$_4$. CH$_3$O* and CH$_2$OH* intermediates can participate in the final hydrogenation step to generate the products, CH$_3$OH and CH$_4$, as illustrated in Figures 4 and S4. During the final hydrogenation process at the V/C interface, the CH$_3$O* intermediate preferentially exothermically binds a proton at the carbon site, forms CH$_3$OH*, and with its oxygen atom, and generates methane. The barrier for this step is as high as 1.47 eV, making it the rate-determining step. CH$_3$O* also can bind a proton at the oxygen site, forming the CH$_3$OH* intermediate, with a 0.77 eV lower barrier. However, the reaction energy for this alternative process is 0.69 eV, and the desorption energy for methanol is 1.21 eV, which makes the process thermodynamically forbidden. Similarly, despite an exothermic production of CH$_3$OH*, with a lower activation energy of 1.04 eV, the CH$_3$OH* intermediate finally results in CH$_4$, because of the strong adsorption of methanol. Thus, only methane is generated at the V/C interface of the defective surface. When this process happens at the S/C interface, the solvent effect slightly enhances the reactions. The enthalpies of all reaction steps decrease by more than 0.1 eV, and the corresponding barriers also have obvious downshifts. Because of the weak adsorption of methanol at the S/C interface, the pathway involving the CH$_3$OH* intermediate is the kinetically favorable one to generate methanol.

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pathway (i.e., the CH₃OH* pathway). On the other hand, at the S/C interface, methanol could be a feasible and kinetically preferred product, produced via CO* → CHO* → CH₂O* → CH₂OH* → CH₃OH* → CH₃OH (i.e., the CH₃OH pathway). To summarize, a scheme of the reactions occurring at the S/C interface is shown in Figure 5, which surprisingly suggests that CO is the most feasible reactant in this reaction, and CO₂, CH₂OH, and CH₄ are the products. However, the main product in these conditions is still methane, because the barriers of producing methane and hydrogenating CO are similar. If there is plenty of formaldehyde yielded by the pristine surface participating in this pathway, the main product should be methanol. This is consistent with the experiments showing that CO₂ reduction reaction on anatase TiO₂ are CO and CH₄ in the gas/solid reaction, but CO, CH₄, and CH₃OH could be generated at the liquid/solid interface. Beyond that, we find that the solvent effect greatly impacts the beginning and the end of a pathway (adsorption and desorption processes), but influences the intermediate steps only slightly.

**Adsorption and Reaction Processes at the Electrolyte/Catalyst (E/C) Interface of the Defective Surface.**

The adsorption energies of all involved reactants and products calculated as a function of $\phi_{\text{SHE}}$ are shown in Figure 6. Because the variation of $\phi_{\text{SHE}}$ is dependent on the applied negative bias, the way we describe the profiles is along the direction of decreasing $\phi_{\text{SHE}}$. To explore the stability of TiO₂ under negative (i.e., reducing) potentials, we ran experimental measurements (see the Supporting Information) using an amorphous TiO₂ catalyst deposited by atomic layer deposition (ALD) over the course of a 10 h reaction. The stability of the simulated system was tested by depositing a 5 nm thick layer of TiO₂ on ITO substrates using ALD. CO₂ reduction was performed in a three-terminal potentiostat for 10 h in 0.5 mol of KCl with pH = 7 buffer solution while continuously bubbling CO₂ through the solution with the working electrode held at −0.6 V vs NHE. Current versus potential measurements were taken before and after the 10 h reaction, as plotted in Figure S6. Here, an increase in the electrochemical current can be observed during the course of

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**Figure 5.** Schematic diagram of the CO₂ (CO) reduction catalytic cycle at the S/C interface on the defective anatase surface. The black arrows illustrate the thermodynamically favorable pathway, and the red arrows show the kinetic favorable pathway. The red and black numbers represent the activation energy and the enthalpy variation of the corresponding reaction steps, respectively.

**Figure 6.** Calculated adsorption energies as a function of applied electrochemical potential. The black solid line is the benchmark of 0 eV.
the measurement, indicating an increase in the O-vacancy concentration due to the applied reducing potentials. X-ray photoelectron spectra (XPS) taken before and after the 10 h reaction provide further evidence for the increase in O-vacancy density. These spectra show an increase in the nonstoichiometric Ti$^{IV}$ states (which correspond to O-vacancies) from 0.031 to 0.048, as indicated in Figure S7. We believe that the increase in Ti$^{IV}$ states is due to the growth of O-vacancies rather than the buildup of the Ti$_2$O$_3$ phase, because it is difficult to convert TiO$_2$ to Ti$_2$O$_3$ electrochemically. The transformation between these two phases entails a very high energy barrier, which requires annealing to be overcome.$^{56-58}$

As seen from Figure 6a, CO$_2$ still cannot exothermically bind to either surface, suggesting the dissolved CO$_2$ has to be converted before taking part in the reaction. CO$_2$ on the other hand, can be adsorbed on the pristine surface within a rather large range of $\phi_{\text{SHE}}$ values. It is also exothermically adsorbed at the O$_v$ site below the $\phi_{\text{SHE}}$ of $-0.28$ V. Therefore, the reactive window is defined from $-0.6$ to $-0.28$ V, where the upper limit depends on the adsorption of the CO species and the lower limit depends on the limitation of the experiment. In terms of the products (Figure 6b), all of them would directly or indirectly desorb from the surface except for the CH$_2$O species, which has a considerable adsorption energy on the defective surface at certain $\phi_{\text{SHE}}$ values.

It is noteworthy that some binding energies exhibit uptrends and others exhibit downtrends as a function of $\phi_{\text{SHE}}$. To elucidate the underlying reason, the charge transfer upon the molecular chemical adsorption at the S/C interface was studied (Table 2), where the positive values indicate the

<table>
<thead>
<tr>
<th>adsorbates</th>
<th>charge transfer from the surface slab/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.28</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.67</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>$-0.16$</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>$-0.19$</td>
</tr>
</tbody>
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<thead>
<tr>
<th>adsorbates</th>
<th>charge transfer from the surface slab/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.88</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.67</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>1.55</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>$-0.2$</td>
</tr>
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corresponding adsorbed molecules are oxidants, while the negative values refer to reductants. Within this definition, carbon oxides are oxidants at both surface sites, and, interestingly, the CH$_2$O at the defective surface is also an oxidant. From Figure 6, it is quite clear that all binding energies of adsorbed oxidants have the same trend of becoming more stable with an increasing bias, and vice versa for the reductants. We think the charge transfer plays an important role in this process. As shown before, the introduced excess charge mainly accumulates at and near the surface of the electrode, which thus becomes more reducing, upon increasing net charge and decreasing $\phi_{\text{SHE}}$. Therefore, the bound oxidants can withdraw more electrons and become more stable. On the other hand, the surface-bound reductants cannot readily donate electrons to the surface and destabilize accordingly. Here, the diffusion process, that is, adsorption and desorption of reactants and products, which is supposedly controlled by $\phi_{\text{SHE}}$, could affect the reaction process. Hence, we think the diffusion process is one factor to determine the onset potential.

The conversion between CO and CO$_2$ at the E/C interface of the pristine surface was calculated (Figure 7). In the existence of the $\phi_{\text{SHE}}$, the CO oxidation process becomes a little more difficult in the beginning ($-0.3$ V) and slightly better ($-0.6$ V) with the increasing negative bias. Under this condition, the CO species still reduces the surface (the S/C interface).

The hydrogenation reactions of CO at the O$_v$ site were studied at the E/C interface below the $\phi_{\text{SHE}}$ value of $-0.28$ V (Figures 8 and 9). At the S/C interface, there are two pathways: a kinetically favorable one that yields CH$_3$OH and the other one forming CH$_4$. The main product should be methane because of the similar barriers of hydrogenating CO and generating CH$_4$. In the presence of $\phi_{\text{SHE}}$ the barrier of the CO hydrogenation has a dramatic drop along the potential (Figure 8a), while the CH$_4$ generation one remains at a certain level (Figure 9a). At the $\phi_{\text{SHE}}$ of $-0.3$ V, for instance, the activation energy of the first hydrogenation step reduces to 1.36 eV (Figure 8b), whereas the CH$_3$O* $\rightarrow$ CH$_4$ energy grows to 1.53 eV (Figure 9b) as compared to the S/C interface. Therefore, the kinetically favorable pathway, that is, the CH$_3$OH pathway, becomes the main process at the E/C interface with an appropriate temperature. The rate-determined step is the first hydrogenation with the activation energy of 1.36 eV at $-0.3$ V. As the negative bias increases, all involved enthalpy variations and activation energies have different changes. At the $\phi_{\text{SHE}}$ value of $-0.45$ V, barriers of the first, second, and CH$_3$O* hydrogenation steps decrease to different degrees (Figures 8c and 9c). Apart from the activation energies, the formation energies change as well, and the CH$_3$O intermediate become more stable, for instance. When the $\phi_{\text{SHE}}$ reaches $-0.6$ V, the barrier of the second hydrogenation step reduces to 1.16 eV (Figure 8d), which is close to the increasing barrier of the CH$_3$OH generation step (0.93 eV, Figure 9d).

Overall, in the presence of a lower applied negative bias, methanol is favored as the final product instead, which is consistent with the experiment.$^{26,28}$

**Deoxygenation Pathway of Methane Generation at the Defective Surface**. Even though the CH$_3$O* pathway in the last section is not competitive with the CH$_3$OH one at the E/C interface, the experiment still found methane being produced.$^{57}$ One possible reason is that methane could be generated at the pristine surface. Alternatively, a deoxygenation pathway involving the removal of oxygen before the initial hydrogenation step, proposed by Ji et al., could be envisioned. However, this pathway has been proven impossible at both the pristine and the defective surface.$^{58,59}$ It is also conceivable that oxygen would dissociate away as a hydroxyl group, rather than O (curing the O$_v$), for fulfilling a catalytic cycle. In our previous work on anatase without solvent or electrochemical potential, the deoxygenation step of the CHOH* intermediate was 1.74 eV uphill and had an activation energy of 1.96 eV, that is, less favorable than the original CH$_3$O* pathway. In this study, a dissociation step of the CH$_3$OH* intermediate was calculated at the S/C interface of the defective surface (Figure 10). The reaction energy of the deoxygenation step decreased to 0.99 eV at the V/C interface of the defective surface, and the corresponding barrier is only 1.10 eV, which is lower than the rate-determined barrier of the CH$_3$O* path. The products of this step are the CH$_3$* intermediate and an OH radical. The OH radical is likely to accept an electron from the cathode and migrate to the counter electrode, and the CH$_3$* intermediate becomes available to participate in the following reaction steps. The hydrogenation steps afterward are downhill, with barriers similar to those of the deoxygenation step, and result in CH$_4$. In the presence of the solvent, both the activation and the
reaction energies of these subsequent steps are slightly lowered (by ca. 0.1 eV), with the exception of the final step, which experiences a 0.04 eV increase in the activation energy. Even though the reaction energy of the deoxygenation step nearly halved, the remainder of the pathway is still too energy-demanding to compete with the CH$_3$O$^*$ pathway at the S/C interface at room temperature.

However, this deoxygenation step is heavily dependent on the $\phi_{SHE}$ according to our calculation on the deoxygenation pathway at the E/C interface of the defective surface (Figure 11). At the $\phi_{SHE}$ value of $-0.3$ V (Figure 11b), the corresponding enthalpy variation drops by 0.81 eV as compared to the S/C interface to make the deoxygenation pathways feasible at room temperature. Meanwhile, the applied bias also exerts a slight negative influence on all involved activation energies. As the bias increases, all influenced barriers suffer a downtrend (Figure 11d), which approaches the barrier of the CH$_3$OH generation step. However, at $-0.6$ V, the rate-
determined step of the deoxygenation pathway is still higher than that of the CH$_3$OH one, which makes the latter the dominant pathway.

In conclusion, the catalytic cycle in the presence of $\phi_{\text{SHE}}$ is such that the adsorbed CO mainly follows the CH$_3$OH pathway that has a rate-determined barrier of 1.16 eV and generates methanol at $-0.6$ V as illustrated in Figure 12. As compared to the CH$_3$OH and deoxygenation pathways at the S/C interface, the pathways are dramatically improved by the applied bias. If there is the formaldehyde species generated from the pristine surface, it would directly occupy the O$_v$ site and produce methanol or methane along the pathways at the E/C interface of the defective surface. Here, the reaction process is controlled by the potential-dependent thermodynamic and kinetic processes, which are thought to be another factor to determine the onset potential.

## CONCLUSIONS

The adsorption and reaction mechanisms involved in the CO$_2$ reduction at both the solvent/catalyst and the electrolyte/catalyst interfaces of the defective anatase TiO$_2$ (101) surface were investigated by DFT. We analyzed the charge distribution at the pristine and defective surface slabs, which are deeply influenced by the solvent and electrochemical potential. We reported the effect of the charge redistributions within the slab on the electronic structures and stabilities of the adsorbed species involved in the reaction in various conditions. We proposed two different catalytic cycles operating at the S/C and the E/C interfaces.

While making a surface cut creates a great onset of ionic bonding character in the surface, the solvent effect is shown to electronically passivate it due to polarization interactions. As a result, the adsorption energies of all involved molecules are weakened in the solvent, as compared to the dry interface. That benefits desorption of products such as methanol, but deters the binding of the reactants such as the carbon oxides. When the surface slab is charged as a cathode, and the solvent becomes an electrolyte, the extra charge concentrates in the surface area, consistent with the behavior of a semiconductor electrode. This redistribution enhances the reducing ability of Ti and reduces the oxidizing ability of O at the surface. The binding of involved chemical species is then further affected at the cathode, based on their redox properties.

The reaction mechanism at the S/C and E/C interfaces of defective surface is found to vary with the change of the reaction conditions. At the S/C interface, CO$_2$ cannot directly adsorb, and instead the produced CO tends to uptake an O atom from the surface, creating O$_v$ and producing more CO$_2$. CO can also bind to the oxygen vacancy and undergo photocatalytic hydrogenation, yielding CH$_4$ and CH$_3$OH, of which the latter is considered not to desorb at the V/C interface.
interface. Interestingly, the CO species is suggested by the calculation to be the main reactant at the S/C interface, forming CO₂, CH₄, and CH₃OH. The solvent effect is found to affect the reaction process only slightly, but greatly impacts the diffusion process.

The mechanisms are controlled by diffusion and reaction processes, which are a function of the applied electrochemical potential at the E/C interface. In the presence of bias, the conversion of CO to CH₃OH as the main product is kinetically favored. The adsorption of the main reactant, CO, is adsorbed under the potential below −0.28 V. Therefore, the onset potential involved in the (photo)electrochemical process is supposed to be controlled by both the diffusion and the reaction processes.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c00947.

Experimental details; (x,y) plane average potential as a function of z value; (x,y) plane charge density difference as a function of z value; all snapshots of configurations; current versus potential plot; current versus time plot; and XPS before and after reaction (PDF)

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**Figure 11.** Electronic free energies as functions of applied electrochemical potential (a) on the deoxygenation pathway and the corresponding snapshots at ϕₛₑₚ values of −0.3 V (b), −0.45 V (c), and −0.6 V (d).

**Figure 12.** Schematic diagram of the CO₂ reduction reaction catalytic cycle at the E/C interface of the defective surface with a ϕₛₑₚ of −0.6 V. The red and black numbers represent the activation energy and the enthalpy variation of the corresponding reaction steps, respectively.
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Notes
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