

# Mechanism of CO<sub>2</sub> Photocatalytic Reduction to Methane and Methanol on Defected Anatase TiO<sub>2</sub> (101): A DFT Study

Ji-Yuan Liu<sup>1,2</sup>, Xue-Qing Gong<sup>2</sup> and Anastassia Alexandrova<sup>1,3,\*</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA, 90095, USA

<sup>2</sup>Key Laboratory for Advanced Materials, Center for Computational Chemistry and Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China.

<sup>3</sup>California NanoSystems Institute, Los Angeles, CA, 90095, USA

Corresponding Author e-mail: [ana@chem.ucla.edu](mailto:ana@chem.ucla.edu)

**ABSTRACT:** With rising emission of CO<sub>2</sub> affecting human life, photocatalytic reduction of CO<sub>2</sub> attracts substantial research interest. Anatase TiO<sub>2</sub> is known to be one of the most promising catalysts of this process. Here, we adopted density functional theory calculations to systematically study the pathways of CO<sub>2</sub> reduction on the defected anatase TiO<sub>2</sub>(101) surface. We find that oxygen vacancies play a critical role in promoting the reaction, as compared to the pristine surface. They help CO<sub>2</sub> binding, activation, and dissociation, and stabilize other reaction intermediates. The most feasible identified reaction mechanism proceeds through surface CO species, to CHO, CHOH, CH<sub>2</sub>OH or CHO, CH<sub>2</sub>O, and CH<sub>3</sub>O, to produce methane and methanol. In addition, there exists a carbene-like deoxygenation pathway to form the CH species on the vacancy, which can give rise to methane by binding protons successively.

## Introduction

Carbon dioxide, mainly emitted from human activities, *e.g.*, the combustion of fossil fuels, is a putative cause of the global warming. To reduce carbon dioxide, many methods such as photocatalytic, electrocatalytic, photoelectrocatalytic reduction, thermoreduction etc. have been widely studied recently.<sup>1-9</sup> Among the ways of conversion of CO<sub>2</sub>, the most attractive one is to use the solar energy and photocatalytically convert CO<sub>2</sub> back to usable organic fuels, such as methanol. Photocatalysis consists of three steps: the solar light harvesting process, the separation and transport of photogenerated electrons and holes, and the reactions at the surface. Photoelectrocatalysis is a powerful technique that has advantages as compared to both photocatalysis, and electrocatalysis. On the one hand, the solar energy consumed in the process can significantly reduce the applied potential, and thus decrease the consumption of electricity. On the other hand, the applied electric potential can help photo-induced electron-hole pair separation, causing the hole migration to the anode where it can participate in the oxidation reaction. Although photo- and photoelectro-catalytic reactions occur in different chemical conditions, the charge transfer mechanism that underlies them is *similar* and consists of transferring electrons to the reactants through the catalyst to facilitate the conversion. However, the details of this mechanism for CO<sub>2</sub> conversion still remain unclear. Therefore, in this paper, we focus on the reaction mechanism in photocatalytic reduction of CO<sub>2</sub>, with the goal of providing an insight into the mechanisms of both photocatalytic and photoelectrocatalytic reduction.

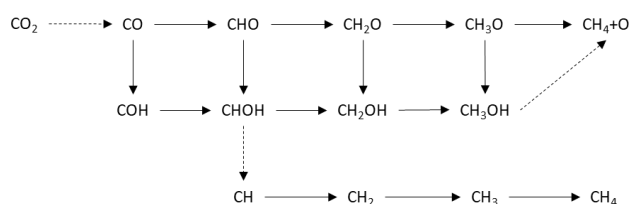
The pioneering study was led by Inoue et al in 1979, first finding that CO<sub>2</sub> could be reduced at the surfaces of several semiconductors, such as titanium

dioxide ( $\text{TiO}_2$ ), under illumination.<sup>10</sup>  $\text{TiO}_2$  has charming properties such as low cost, stability, and a large band gap, and is widely studied experimentally and theoretically for the  $\text{CO}_2$  reduction.<sup>11-20</sup>  $\text{TiO}_2$  has three common phases, rutile, anatase, and brookite.<sup>21</sup> Among these phases, rutile and anatase are investigated most widely investigated. Additionally, because the rate of electron-hole recombination in anatase (101) is more than 10 times smaller than in rutile (110)<sup>22</sup>, the anatase phase has a better performance in the photo-driven charge transfer system. The anatase phase of  $\text{TiO}_2$  has two common facets, (001) and (101), where the (101) is the thermodynamically most stable one<sup>23</sup>. Yu et al.<sup>13</sup> suggested that the (101) facet should be the reactive surface in photocatalytic reactions because it has a lower conduction band edge. The (001) facet can trap holes and transfer electrons to the (101) surface, to prepare its reduced state for the reduction of  $\text{CO}_2$ . Therefore, anatase  $\text{TiO}_2$  (101) is considered the reactive surface through this study.

Over recent years, the reduction of  $\text{CO}_2$  to methane and methanol on pristine anatase  $\text{TiO}_2$  has been widely investigated theoretically. He et al. was the first one who calculated the conversion of  $\text{CO}_2$  to  $\text{HCOOH}$  on titania, and claimed a two-electron mechanism of the formation of formic acid from carbon dioxide.<sup>15,16</sup> The study by Ji et al. followed this direction, extending the results to the formation of  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$ , and verified the importance of oxygen vacancy on the surface.<sup>19,20</sup> Ip et al. analyzed the probabilities of carbene, formaldehyde, and glyoxal pathways suggested by experiment.<sup>18</sup>

Indeed, anatase is highly prone to having defects, such as oxygen vacancies,  $\text{O}_v$ , as well as forming amorphous structures. It was furthermore shown that the presence of  $\text{O}_v$  is essential for explaining the activity of anatase in photocatalytic applications.<sup>24,25</sup> Even though Ji et al already studied some parts of the pathway working on defective surface, there are still blanks remaining, and the present study fills some of them.

In our work, the photocatalytic process of  $\text{CO}_2$  reduction on the (101) facet of anatase  $\text{TiO}_2$  with an oxygen vacancy, was simulated. One hydrogen atom was introduced into the system at each photocatalytic step. The electron from adsorbed hydrogen atom can spontaneously move to surface producing a proton and an electron in the surface, as proved by both theory<sup>26</sup> and experiment<sup>27</sup>. Hence, the introduced hydrogen can be separated into  $\text{H}^+$  and  $\text{e}^-$  participating in consecutive reaction steps. Because no experimental evidence of multielectron-transfer process was found for photocatalysis on semiconductors,<sup>28</sup> and also, one electron step has been reported before<sup>11</sup>, we investigated the pathways proceeding through one-electron process, based on Scheme 1, where solid arrows represent hydrogenation steps.



**Scheme 1.** Perspective pathway from  $\text{CO}_2$  to  $\text{CH}_4/\text{CH}_3\text{OH}$ . Solid arrows represent hydrogenation step, while dash arrow represents a reduction step.

## Computational Details

All DFT+U calculations were performed with the Vienna Ab initio Simulation Package (VASP).<sup>29-32</sup> The projector augment wave (PAW)<sup>33,34</sup> method with the Perdew, Burke and Ernzerhof (PBE)<sup>35</sup> functional was used to optimize the lattice parameters and relax the structures. A 400 eV plane-wave cut-off energy and spin polarization were set, and the residual force components on

each atom were lower than  $0.03 \text{ eV}\cdot\text{\AA}^{-1}\cdot\text{atom}^{-1}$ . The Tkatchenko-Scheffler dispersion correction method<sup>36</sup> was adopted. The effective parameter of coulomb interaction correction of Ti atoms,  $U_{\text{eff}}$ , was set as 3.5 eV, which has been studied in our previous work.<sup>37</sup> The k-mesh of  $2 \times 2$  was utilized. **Bader charge analysis was considered on adsorption configurations.**<sup>38</sup> The climbing image nudged elastic band (cNEB) method was utilized for transition state search.<sup>39</sup> All the transition state geometries were confirmed by phonon calculations, and each had just one imaginary mode aligned with the reaction coordinate.

The surface slab was made by cleaving a  $(3 \times 1)$  supercell of optimized anatase  $\text{TiO}_2$  bulk as a (101) surface, with an oxygen atom removed from the middle of top layer, as shown in Figure 1. The best number of layers was tested as shown in Table S1. It converged at four O-Ti-O layers with the bottom two layers frozen. The vacuum layer was 15 Å thick. In our earlier study<sup>37</sup>, as well as in the recent paper by Ko et al<sup>40</sup>, it was shown that a fairly large unit cell, as well as the carefully chosen level of theory (the DFT functional, Hubbard U correction, and inclusion of dispersion) are required to produce meaningful results for defected anatase.

All the adsorption and desorption energies were calculated by using the following formula:

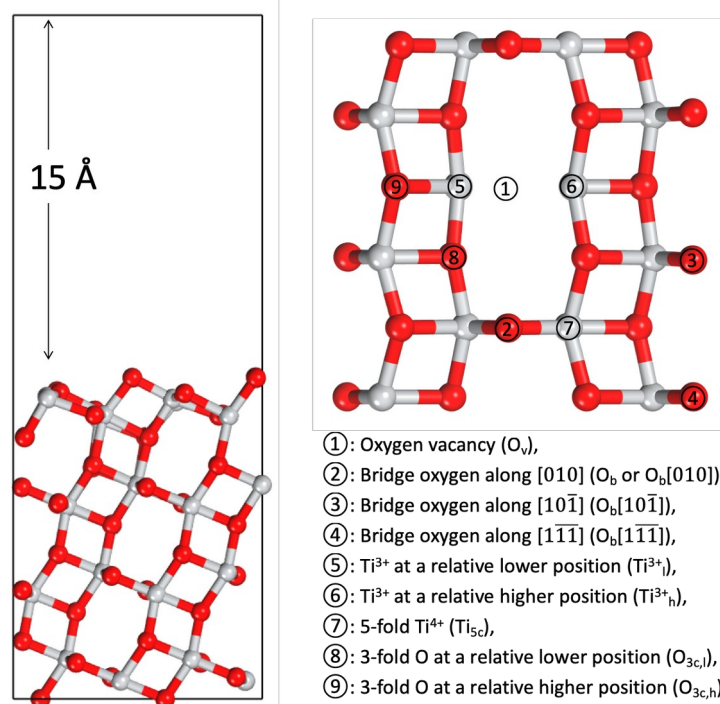
$$E_{\text{ads}} = -E_{\text{des}} = E(\text{adsorbate@slab}) - E(\text{slab}) - E(\text{adsorbate})$$

Where  $E$  stands for DFT+U calculated energy in eV, and  $E_{\text{ads}}$ ,  $E_{\text{des}}$  are energies of adsorption and desorption, respectively.

During the specific illumination on  $\text{TiO}_2$ , electron-hole pairs keep being separated and recombining. Holes combine with water molecules to produce protons, hydroxyl groups, and oxygen, while electrons and protons generated from the holes take part in the reduction reaction. Because reactions are multi-step, to align the energy with different number of protons and electrons, the following formula was used:

$$E'_{\text{state}} = E_{\text{state}} - n(H) \cdot E_{\text{ads}}(H)$$

Where  $E_{\text{state}}$ ,  $E'_{\text{state}}$  are the original and aligned energies of a same state (initial, transition, intermediate, or final), respectively, and  $n(H)$  is the number of hydrogen atoms in that state.  $E_{\text{ads}}(H)$  represents for the energy of single hydrogen atom adsorbed on the oxygen defective (101) slab. All the energies of reaction states are shown as  $E'_{\text{state}}$ . The absolute aligned energy differences between with and without new introduced hydrogen atom of the same configuration are within 0.08 eV. [There is only one exception and we will discuss it in the section C Pathway.](#)



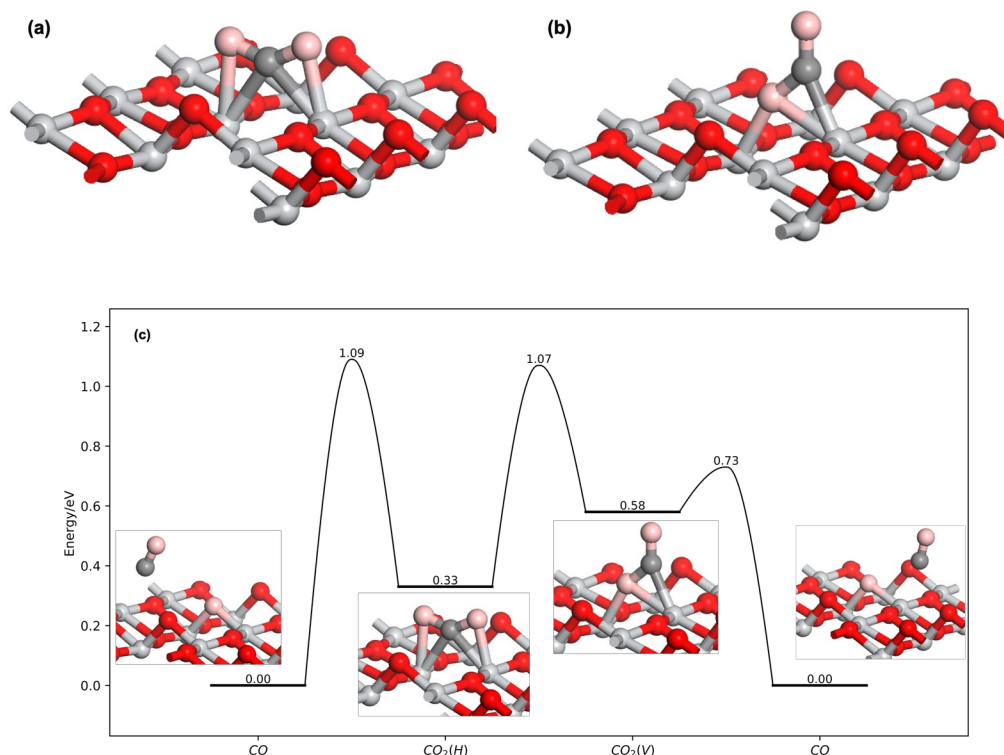
**Figure 1.** The side (left) and top (right) view of the anatase  $TiO_2$  (101) surface slab. The silver and red spheres represent the Ti and O, respectively.  $O_v$ ,  $O_b$ ,  $O_b[010]$ ,  $O_b[10\bar{1}]$ ,  $O_b[1\bar{1}\bar{1}]$ ,  $Ti^{3+l}$ ,  $Ti^{3+h}$ ,  $Ti_{5c}$ ,  $O_{3c,l}$  and  $O_{3c,h}$  are illustrated respectively.

## Results & discussion

### Adsorption and dissociation of $CO_2$ reduction

When adsorbing on anatase, the  $CO_2$  molecule bends, and binds to the  $O_v$  either “horizontally” as a  $CO_2(H)$  site with an adsorption energy of -0.89 eV (Figure 2a), or “vertically”, occupying the vacancy as a  $CO_2(V)$  with an adsorption energy of -0.65 eV, as shown in Figure 2b. Both adsorption energies are larger than that corresponding to the most stable configuration of  $CO_2$  on the pristine anatase (101) surface (-0.45 eV) (Figure S1). This suggests that  $CO_2$  likely occupies the vacancy site. Charge transfer approves this result as well. It shows that in  $CO_2(H)$ ,  $CO_2$  molecule accepts 0.84 e from surface slab, in which 0.76 e was distributed to C and 0.38 e was contributed by  $Ti^{3+}$  around the vacancy, while in  $CO_2(V)$ ,  $CO_2$  accepts a little bit less electron of 0.83 e, in which 0.40 e was contributed by  $Ti^{3+}$  and 0.73 e was distributed to C. It's obvious that rather than O atom, the transferred electrons prefer to be localized on C atom. Moreover, it seems  $CO_2$  becomes more stable when C receives more electron. This could be attributed to extra electrons make  $CO_2$  bend easily and stable. Charge density plots (Figure S2a for  $CO_2(H)$  and S2b for  $CO_2(V)$ ) illustrate the transition metal's d orbitals play an important role in activating  $CO_2$  molecules. From the computed potential surface (Figure 2c) and transition states (Figure S3), we find that  $CO_2(H)$  needs to overcome a significant barrier of 0.74 eV to transform to  $CO_2(V)$ . Meanwhile, a similar activation energy of 0.76 eV is required to form CO; note that our number is a little bit higher than the barrier previously reported by Sorescu et al.,<sup>41</sup> likely because we computed a single step reaction from  $CO_2(H)$  to CO, whereas it is a two-step process in their work. From  $CO_2(V)$ , only 0.15 eV activation energy is needed to form CO, which is quite a bit lower

than that from CO<sub>2</sub>(H). Both pathways cure the O<sub>v</sub>, consistently with the experimental work.<sup>12</sup>



**Figure 2.** Configurations of adsorbed CO<sub>2</sub> on O<sub>v</sub> site: (a): CO<sub>2</sub>(H); (b): CO<sub>2</sub>(V). (c): Adsorption and dissociation of CO<sub>2</sub> on the oxygen vacancy site. The silver, red, pink and grey spheres represent the Ti, O, O in CO<sub>2</sub> and C, respectively.

### Adsorption of hydrogen on pristine and defected anatase TiO<sub>2</sub> (101) surface

The adsorption of hydrogen, the electron and proton source, was also studied before introduced into the system. For pristine slab, there are three different sites to activate hydrogen for binding, O<sub>b</sub>, O<sub>3c,h</sub> and O<sub>3c,l</sub>. Based on bader charge analysis, the average localized electrons on O<sub>3c,h</sub> is 0.018 more than O<sub>3c,l</sub>, and the  $E_{ads}(H)$  on O<sub>3c,h</sub> is accordingly less stable of 0.11 eV than O<sub>3c,l</sub> (shown in Table 1), otherwise the electron on hydrogen cannot be transferred to the surface. The hydrogen average binding energy is -2.68 eV on the O<sub>b</sub>, which is far more stable than those on O<sub>3c</sub>. In terms of the defected surface, more sites such as the O<sub>b</sub> along different directions need to be considered. The average  $E_{ads}(H)$  on different O<sub>b</sub> and O<sub>3c</sub> are rather close to those on pristine slab. Interestingly, Ti<sup>3+</sup> could be another new anchor point for atomic hydrogen binding on, with an adsorption energy of -2.72 eV, which is at a similar level as O<sub>b</sub>. Therefore, hydrogen would like to evenly diffuse to each O<sub>b</sub> and Ti<sup>3+</sup> sites and O<sub>b</sub>[010] is reasonably set as a mount point for introducing hydrogen.

Table 1. The adsorption of hydrogen on pristine and defected anatase TiO<sub>2</sub> (101) surface slab.

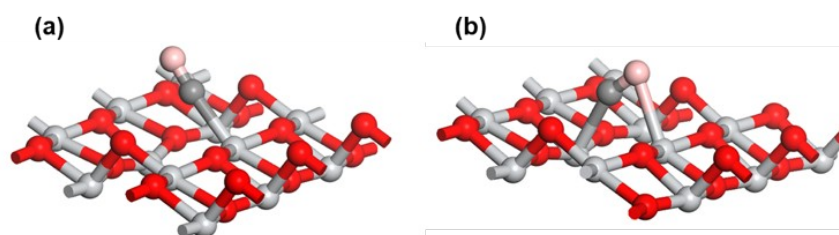
Adsorption site	Adsorption energy/eV
O <sub>b</sub> @pristine	-2.68 <sup>a</sup>

$O_{3c, h}@pristine$	-1.88
$O_{3h, l}@pristine$	-1.98
$Ti_{5c}@pristine$	N/A
$O_b[010]@defected$	-2.65 <sup>a</sup>
$O_b[10\bar{1}]@defected$	-2.69 <sup>a</sup>
$O_b[11\bar{1}]@defected$	-2.62 <sup>a</sup>
$O_{3c, h}@defected$	-1.89
$O_{3c, l}@defected$	-2.00
$Ti^{3+}_h@defected$	-2.42
$Ti^{3+}_l@defected$	-2.72

a: All energies marked with a superscript 'a' represent an average energy among a few similar configurations.

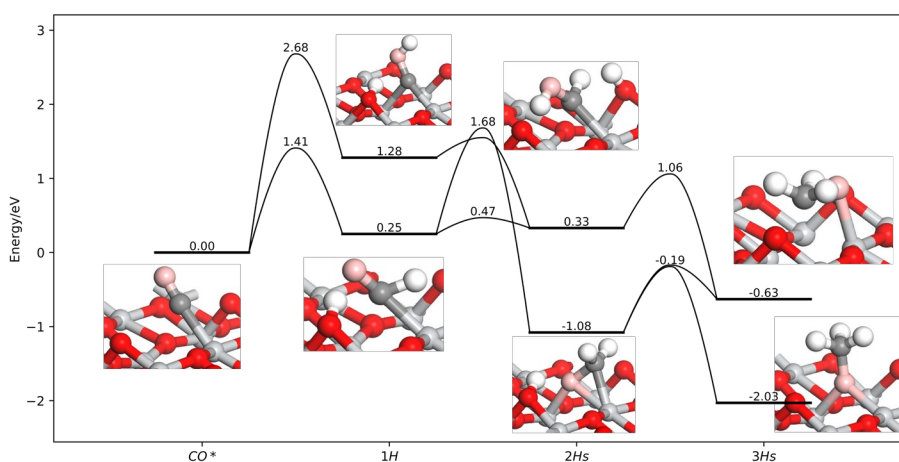
### Adsorption of CO on oxygen vacancy

The pathways of HCOOH being obtained from CO<sub>2</sub> or CO on pristine anatase surface have been investigated before<sup>16,19</sup> and CO was reported<sup>19</sup> cannot bind to the pristine surface, hence, we focused on the role of O<sub>v</sub> in the reduction reaction. Since only a part of catalytic cycle was investigated in this article, the recovery of O<sub>v</sub> would not be discussed. The adsorption of CO on O<sub>v</sub> site is shown in Figure 3a and 3b. There are two initial adsorption configurations. The one, named CO(A), has only the C atom binding to Ti<sup>3+</sup>, and it is more stable, with the adsorption energy of -0.97 eV. The configuration called CO(B), features the bidentate binding to the surface and has a smaller adsorption energy of -0.48 eV. We can see that the CO(A) configuration has a stronger adsorption to anatase (101) than CO<sub>2</sub>(H), suggesting that CO is going to strongly compete with CO<sub>2</sub> binding to the O<sub>v</sub> site. Charge analysis also supported this. C gains 0.38 e in CO(A) and 0.37 e in CO(B), respectively. Besides, the length of C-O and C-Ti in CO(A) are 1.16 and 2.18 Å, which are shorter than corresponding bond lengths in CO(B) as 1.18 and 2.32 Å, suggesting the adsorption of CO(A) is more stable.



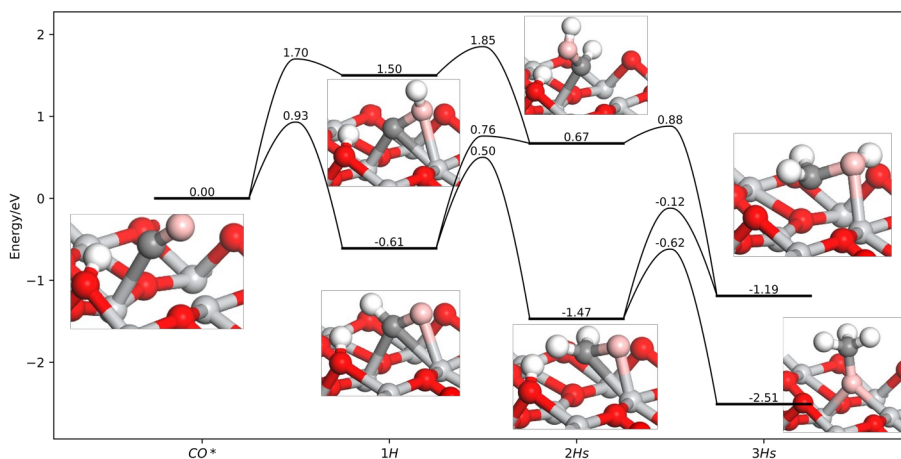
**Figure 3.** Adsorption of CO on the oxygen vacancy site. (a) the more stable monodentate configuration CO(A) with C binding to Ti<sup>3+</sup>; (b) the less stable bidentate configuration CO(B). The silver, red, pink and grey spheres represent the Ti, O, O in CO and C, respectively.

Hydrogenation was studied from these two initial points separately. As described before, only one hydrogen atom was introduced into the system per reaction step and adsorbed on the O<sub>b</sub> site to participate in the photocatalytic reduction.



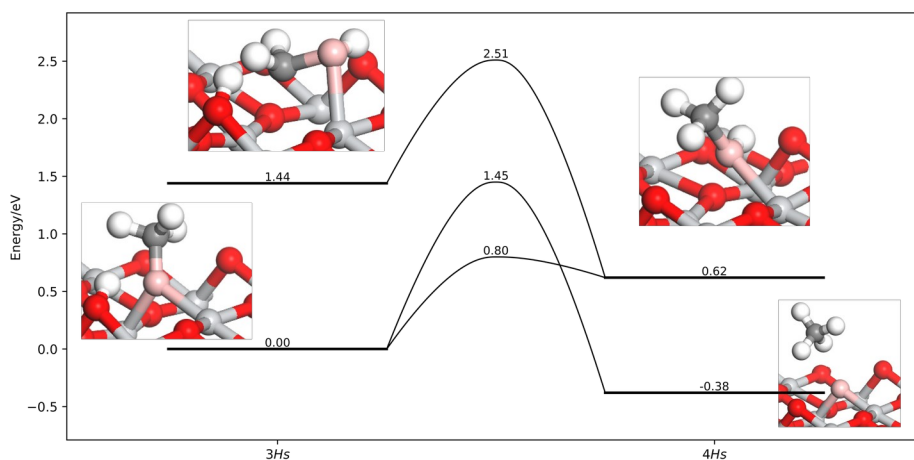
**Figure 4.** The computed reaction pathway starting from configuration CO(A) and yielding the methyl species bound to the surface. The  $CO^*[nH(s)]$  labels on x-axis represents the configurations in this column contain extra adsorbed CO [ $n$  hydrogen atom(s)].

First, we consider the reduction of CO by binding  $H^+$  starting from the configuration CO(A) (Figure 4). The barrier to binding  $H^+$  to O in CO is much higher than that to binding H to C. It is not surprising, because the oxygen atom in CO(A) is far away from the  $O_b$  site holding  $H^+$ , and thus proton binding must proceed through an energetically-costly radical mechanism, shown in Figure S5. The total energy of the forming COH species is higher than that of CHO, suggesting that CHO might be the main product in the first hydrogenated step starting from CO(A). In the second step, regardless of the intermediate formed in the first step from which the reaction begins, the CHOH intermediate forms preferentially over  $CH_2O$ , even though  $CH_2O$  is much more stable. The barrier is only 0.22 eV to hydrogenate CHO to CHOH, while the barrier to form  $CH_2O$  is 1.43 eV, which is greater than the total barrier of 0.81 eV to hydrogenate CHO to the  $CH_2OH$  intermediate. Additionally, although the pathways of  $CHOH \rightarrow CH_2OH$  and  $CH_2O \rightarrow CH_3$  are both exothermic, the barriers to the former (0.73 eV) is smaller than that to the latter (0.89 eV). This suggests that  $CH_2OH$  is a more favorable intermediate to form along the pathway starting from the configuration CO(A), with the rate determining step being the first hydrogenated step.



**Figure 5.** The computed pathways starting from configuration CO(B).

The CO(B) configuration will go through a same transition state as CO(A)  $\rightarrow$  CHO with a barrier of 0.93 eV (Figure 5 and [S6 for transition state](#)). Notably, the activation energy of the CO(B)  $\rightarrow$  COH process is 0.5 eV lower than that starting from CO(A). The distance between the O atom of CO(B) and H<sup>+</sup> situated on O<sub>b</sub> is 4.0 Å, i.e. large and only marginally smaller than that in the CO(A) pathway (4.13 Å). The more favorable barrier should have to do with the available relay point reported before<sup>42,43</sup>. Even though the distances to H<sup>+</sup> are similar, the O atom in CO(B) is relatively closer to the surface, and the proton can move O<sub>3c</sub> between Ti<sup>4+</sup> and Ti<sup>3+</sup>, the relay point. Thus, hydrogenating the O atom of CO does not require the formation of the H-radical. The barrier of the CO(B)  $\rightarrow$  CHO process is considerably more competitive than even that of the CO(A)  $\rightarrow$  COH process. If the proton binds to C in CO, the subsequent pathways from CHO to CH<sub>3</sub>O are downhill for either configuration, and the barriers are 0.89 eV and 0.85 eV, for CO(A) and CO(B) being the starting points, respectively. The CH<sub>2</sub>OH intermediate formed from CO(B) is identical to that formed from CO(A). Hence, these two reaction profiles merge in the last hydrogenation step, as shown in Figure 6 [and S7](#).

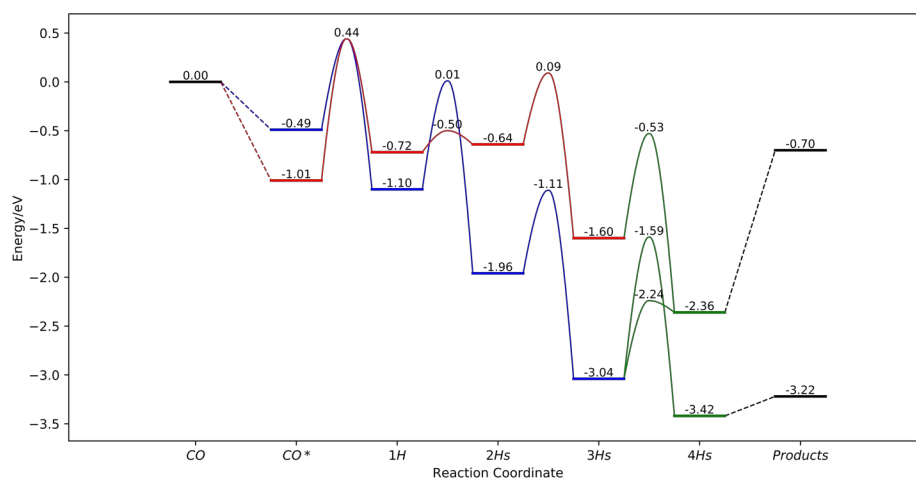


**Figure 6.** The combined computed pathways leading to methane and methanol



We can see that the CH<sub>2</sub>OH intermediate overcomes a barrier of 1.07 eV to form a methanol molecule adsorbed on the O<sub>v</sub> site. However, we found the desorption energy for methanol to be as high as 1.66 eV, making it hard for the adsorbate to desorb from O<sub>v</sub> at room temperature. Additionally, the barrier from the adsorbed methanol (CH<sub>3</sub>OH\*) to CH<sub>3</sub> is quite low (0.18 eV). Therefore, the formation of the CH<sub>3</sub> intermediate is more favorable than the desorption of CH<sub>3</sub>OH. The activation energy of 1.45 eV is needed to produce methane from CH<sub>3</sub>. The desorption energy of methane is only 0.20 eV, indicating that it can easily escape the surface. The process is quite consistent with the experiment, showing that only CO and CH<sub>4</sub> formed during a room temperature photocatalysis,<sup>14,44</sup> and other theoretical claims<sup>20</sup>.

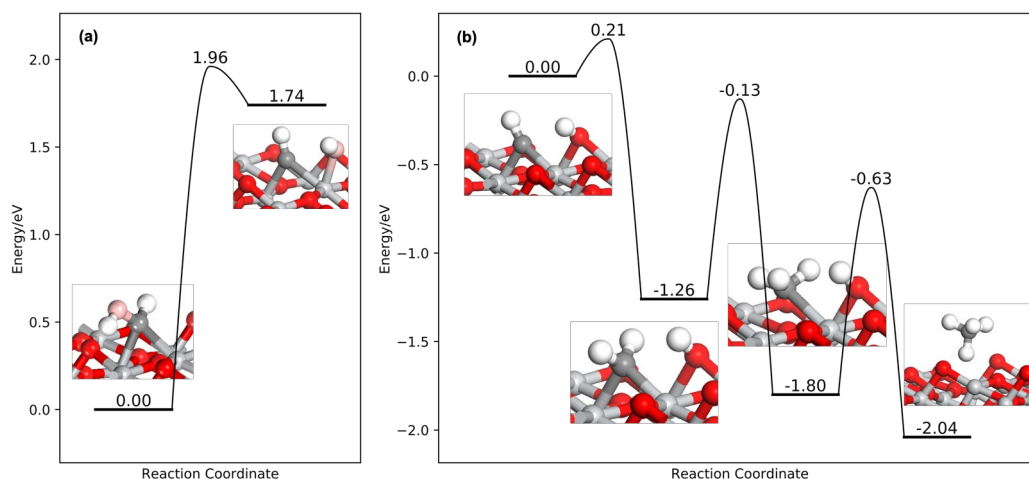
In a conclusion, the overall most favorable pathway from adsorbed CO is CO(A) → CHO → CHOH → CH<sub>2</sub>OH → CH<sub>3</sub>OH\* → CH<sub>3</sub>O → CH<sub>4</sub> or CO(A) → CO(B) → CHO → CH<sub>2</sub>O → CH<sub>3</sub>O → CH<sub>4</sub>. Only CH<sub>4</sub> is expected to be observed at the room temperature as the reaction product. The whole reaction profile is outlined in Figure 7.



**Figure 7.** The overall potential energy surface from CO to CH<sub>4</sub>. Black, red, blue and green bars and curves represent a desorption state, the most favorable pathway for CO(A), the most favorable pathway for CO(B) and pathways after merged, respectively.

### C pathway

Beyond the normal possible pathways of CO, we also found a deoxygenated shortcut to CH<sub>4</sub>. Even though Ji et al<sup>20</sup> dismissed this possible mechanism because of the 2.17 eV CO dissociation energy, we nevertheless pursued the search for the possible carbene-like pathway, following the experimental claims.<sup>45</sup> Our calculations indicate that CH can form by dissociation of the CHOH intermediate along the CO(A) pathway, with the activation barrier of 1.96 eV, as shown in Figure 8a and S8. The process is endothermic by 1.74 eV, which is much lower than that reported in Ji's work. The hydroxyl group formed through dissociation is then able to combine with protons on the surface to form water, or with holes to form oxygen molecule leaving the system while protons would stay on the surface to continue the reaction.



**Figure 8.** (a) The dissociation of CHO species on oxygen vacancy site. (b) The pathway from CH to CH<sub>4</sub>

As illustrated in Figure 8b, the barrier of the first hydrogenation step is 0.21 eV, which means the CH intermediate can be easily hydrogenated with the first proton. In this configuration, we found that the difference using our correction was as high as 0.42 eV, while involving two extra hydrogens, it became 0.22 eV. When three extra hydrogens introduced, *i.e.* there are CH adsorbate and three H atoms on the defected surface slab, the difference shrink to 0.03 eV, which indicated two extra hydrogens' system should be the initial point in this pathway. This may be attributed to a plenty of electrons were needed to breed a bare carbon to stabilize it. The subsequent hydrogenation steps are downhill, proceeding through a series of steps with the average activation energy of around 1.15 eV, to finally produce methane. Overall, this pathway from CHO to CH<sub>4</sub> looks thermodynamically quite favorable. Therefore, the direct deoxygenation and hydrogenation pathway is CO<sub>2</sub> → CO(A) → CHO → CHO(H) → CH → CH<sub>2</sub> → CH<sub>3</sub> → CH<sub>4</sub>, where the rate-limiting step is CHO(H) → CH with a barrier of 1.96 eV.

## CONCLUSIONS

We systematically investigated the mechanism of conversion of CO<sub>2</sub> to CH<sub>4</sub> on defected anatase TiO<sub>2</sub> (101) and found that the two most plausible pathways are CO<sub>2</sub> → CO(A)(CO(B)) → CHO(CHO) → CHO(H)(CH<sub>2</sub>O) → CH<sub>2</sub>OH(CH<sub>3</sub>O) → CH<sub>3</sub>OH\* or CH<sub>4</sub>. The desorption energy of CH<sub>3</sub>OH is -1.66 eV, indicating that if it forms, it would be rather stable on the surface at room temperature. Our results suggest that the hydrogenated CO on the O<sub>v</sub> site will eventually be reduced to CH<sub>4</sub> in the room temperature in the gas/solid heterogeneous condition. O<sub>v</sub> plays a role of activating CO<sub>2</sub> and CO and support intermediates for hydrogen to attack. Beyond that, a hydrocarbon intermediate can be dissociated from the CHO(H) intermediate, which is formed along the pathway on the O<sub>v</sub> site and can go through a downhill pathway reduced into CH<sub>4</sub>. It is noteworthy that even though all the pathways from CO<sub>2</sub> are thermodynamically favorable, the barriers between the steps remain high, especially in the carbene-like pathway. Introducing electric field or electrochemical potential may be the way to accelerate the reaction and improve the yield. We will keep focusing on different ways to decrease those high activation energies.

## Associated Contents

### Supporting Information

The Geometries of transition states and most stable adsorbed CO<sub>2</sub> on pristine slab, charge difference and coordinate files are listed in the supporting information.

## Acknowledgments:

Financial support comes from the CSC Fellowship to J.L. and the NSF-CAREER Award CHE-1351968 to A.N.A.. We also acknowledge the UCLA-IDRE cluster Hoffman2 and XSEDE for computational resources.

## Reference:

- (1) Costentin, C.; Robert, M.; Savéant, J.-M. Catalysis of the Electrochemical Reduction of Carbon Dioxide. *Chem. Soc. Rev.* **2013**, *42*, 2423–2436.
- (2) Habisreutinger, S. N.; Schmidt-Mende, L.; Stolarczyk, J. K. Photocatalytic Reduction of CO<sub>2</sub> on TiO<sub>2</sub> and Other Semiconductors. *Angew. Chem. Int. Ed.* **2013**, *52*, 7372–7408.
- (3) Corma, A.; Garcia, H. Photocatalytic Reduction of CO<sub>2</sub> for Fuel Production: Possibilities and Challenges. *J. Catal.* **2013**, *308*, 168–175.
- (4) Ma, S.; Lan, Y.; Perez, G. M. J.; Moniri, S.; Kenis, P. J. A. Silver Supported on Titania as an Active Catalyst for Electrochemical Carbon Dioxide Reduction. *ChemSusChem.* **2018**, *7*, 866–874.
- (5) Yan, Y.; Han, M.; Konkin, A.; Koppe, T.; Wang, D.; Andreu, T.; Chen, G.; Vetter, U.; Morante, J. R.; Schaaf, P. Slightly Hydrogenated TiO<sub>2</sub> with Enhanced Photocatalytic Performance. *J. Mater. Chem. A.* **2014**, *2*, 12708–12716.
- (6) Xie, S.; Zhang, Q.; Liu, G.; Wang, Y. Photocatalytic and Photoelectrocatalytic Reduction of CO<sub>2</sub> Using Heterogeneous Catalysts with Controlled Nanostructures. *Chem. Commun.* **2015**, *52*, 35–59.
- (7) Chang, X.; Wang, T.; Gong, J. CO<sub>2</sub> Photo-Reduction: Insights into CO<sub>2</sub> Activation and Reaction on Surfaces of Photocatalysts. *Energy Env. Sci.* **2016**, *9*, 2177–2196.
- (8) Li, K.; Peng, B.; Peng, T. Recent Advances in Heterogeneous Photocatalytic CO<sub>2</sub> Conversion to Solar Fuels. *ACS Catal.* **2016**, *6*, 7485–7527.
- (9) Peng, C.; Reid, G.; Wang, H.; Hu, P. Perspective: Photocatalytic Reduction of CO<sub>2</sub> to Solar Fuels over Semiconductors. *J. Chem. Phys.* **2017**, *147*, 030901.
- (10) Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. Photoelectrocatalytic Reduction of Carbon Dioxide in Aqueous Suspensions of Semiconductor Powders. *Nature* **1979**, *277*, 637–638.
- (11) Lee, J.; Sorescu, D. C.; Deng, X. Electron-Induced Dissociation of CO<sub>2</sub> on

- TiO<sub>2</sub>(110). *J. Am. Chem. Soc.* **2011**, *133*, 10066–10069.
- (12) Liu, L.; Zhao, C.; Li, Y. Spontaneous Dissociation of CO<sub>2</sub> to CO on Defective Surface of Cu(I)/TiO<sub>2</sub>-x Nanoparticles at Room Temperature. *J. Phys. Chem. C* **2012**, *116*, 7904–7912.
- (13) Yu, J.; Low, J.; Xiao, W.; Zhou, P.; Jaroniec, M. Enhanced Photocatalytic CO<sub>2</sub>-Reduction Activity of Anatase TiO<sub>2</sub> by Coexposed {001} and {101} Facets. *J. Am. Chem. Soc.* **2014**, *136*, 8839–8842.
- (14) Liu, L.; Jiang, Y.; Zhao, H.; Chen, J.; Cheng, J.; Yang, K.; Li, Y. Engineering Coexposed {001} and {101} Facets in Oxygen-Deficient TiO<sub>2</sub> Nanocrystals for Enhanced CO<sub>2</sub> Photoreduction under Visible Light. *ACS Catal.* **2016**, *6*, 1097–1108.
- (15) He, H.; Zapol, P.; Curtiss, L. A. A Theoretical Study of CO<sub>2</sub> Anions on Anatase (101) Surface. *J. Phys. Chem. C* **2010**, *114*, 21474–21481.
- (16) He, H.; Zapol, P.; Curtiss, L. A. Computational Screening of Dopants for Photocatalytic Two-Electron Reduction of CO<sub>2</sub> on Anatase (101) Surfaces. *Energy Environ. Sci.* **2012**, *5*, 6196.
- (17) Liu, C.; He, H.; Zapol, P.; Curtiss, L. A. Computational Studies of Electrochemical CO<sub>2</sub> Reduction on Subnanometer Transition Metal Clusters. *Phys Chem Chem Phys* **2014**, *16*, 26584–26599.
- (18) Ip, C. M.; Troisi, A. A Computational Study of the Competing Reaction Mechanisms of the Photo-Catalytic Reduction of CO<sub>2</sub> on Anatase(101). *Phys. Chem. Chem. Phys.* **2016**, *18*, 25010–25021.
- (19) Ji, Y.; Luo, Y. Theoretical Study on the Mechanism of Photoreduction of CO<sub>2</sub> to CH<sub>4</sub> on the Anatase TiO<sub>2</sub> (101) Surface. *ACS Catal.* **2016**, *6*, 2018–2025.
- (20) Ji, Y.; Luo, Y. New Mechanism for Photocatalytic Reduction of CO<sub>2</sub> on the Anatase TiO<sub>2</sub> (101) Surface: The Essential Role of Oxygen Vacancy. *J. Am. Chem. Soc.* **2016**, *138*, 15896–15902.
- (21) Diebold, U. The Surface Science of Titanium Dioxide. *Surf. Sci. Rep.* **2003**, *48*, 53–229.
- (22) Maity, P.; Mohammed, O. F.; Katsiev, K.; Idriss, H. Study of the Bulk Charge Carrier Dynamics in Anatase and Rutile TiO<sub>2</sub> Single Crystals by Femtosecond Time-Resolved Spectroscopy. *J. Phys. Chem. C* **2018**, *122*, 8925–8932.
- (23) Lazzeri, M.; Vittadini, A.; Selloni, A. Structure and Energetics of Stoichiometric TiO<sub>2</sub> Anatase Surfaces. *Phys. Rev. B* **2001**, *63*.
- (24) Qiu, J.; Zeng, G.; Ha, M.-A.; Ge, M.; Lin, Y.; Hettick, M.; Hou, B.; Alexandrova, A. N.; Javey, A.; Cronin, S. B. Artificial Photosynthesis on TiO<sub>2</sub> -Passivated InP Nanopillars. *Nano Lett.* **2015**, *15*, 6177–6181.
- (25) Qiu, J.; Zeng, G.; Ha, M.-A.; Hou, B.; Mecklenburg, M.; Shi, H.; Alexandrova, A. N.; Cronin, S. B. Microscopic Study of Atomic Layer Deposition of TiO<sub>2</sub> on GaAs and Its Photocatalytic Application. *Chem. Mater.* **2015**, *27*, 7977–7981.
- (26) Islam, M. M.; Calatayud, M.; Pacchioni, G. Hydrogen Adsorption and

- Diffusion on the Anatase TiO<sub>2</sub>(101) Surface: A First-Principles Investigation. *J. Phys. Chem. C* **2011**, *115*, 6809–6814.
- (27) Panayotov, D. A.; Yates, J. T. N-Type Doping of TiO<sub>2</sub> with Atomic Hydrogen-Observation of the Production of Conduction Band Electrons by Infrared Spectroscopy. *Chem. Phys. Lett.* **2007**, *436*, 204–208.
- (28) Kamat, P. V. Manipulation of Charge Transfer Across Semiconductor Interface. A Criterion That Cannot Be Ignored in Photocatalyst Design. *J. Phys. Chem. Lett.* **2012**, *3*, 663–672.
- (29) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47*, 558–561.
- (30) Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal-Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B* **1994**, *49*, 14251–14269.
- (31) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- (32) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (33) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- (34) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (35) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (36) Tkatchenko, A.; Scheffler, M. Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett.* **2009**, *102*, 073005.
- (37) Ha, M.-A.; Alexandrova, A. N. Oxygen Vacancies of Anatase(101): Extreme Sensitivity to the Density Functional Theory Method. *J. Chem. Theory Comput.* **2016**, *12*, 2889–2895.
- (38) Tang, W.; Sanville, E. and Henkelman, G. A grid-based Bader analysis algorithm without lattice bias, *J. Phys.: Condens. Matter*, **2009**, *21*, 084204
- (39) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J. Chem. Phys.* **2000**, *113*, 9901–9904.
- (40) Ko, K. C.; Bromley, S. T.; Lee, J. Y.; Illas, F. Size-Dependent Level Alignment between Rutile and Anatase TiO<sub>2</sub> Nanoparticles: Implications for Photocatalysis. *J. Phys. Chem. Lett.* **2017**, *8*, 5593–5598.
- (41) Sorescu, D. C.; Al-Saidi, W. A.; Jordan, K. D. CO<sub>2</sub> Adsorption on TiO<sub>2</sub> (101) Anatase: A Dispersion-Corrected Density Functional Theory Study. *J. Chem. Phys.* **2011**, *135*, 124701.
- (42) Kajita, S.; Minato, T.; Kato, H. S.; Kawai, M.; Nakayama, T. First-Principles

- Calculations of Hydrogen Diffusion on Rutile  $\text{TiO}_2(110)$  Surfaces. *J. Chem. Phys.* **2007**, *127*, 104709.
- (43) Li, S.-C.; Zhang, Z.; Sheppard, D.; Kay, B. D.; White, J. M.; Du, Y.; Lyubinetsky, I.; Henkelman, G.; Dohnálek, Z. Intrinsic Diffusion of Hydrogen on Rutile  $\text{TiO}_2(110)$ . *J. Am. Chem. Soc.* **2008**, *130*, 9080-9088.
- (44) Liu, L.; Zhao, H.; Andino, J. M.; Li, Y. Photocatalytic  $\text{CO}_2$  Reduction with  $\text{H}_2\text{O}$  on  $\text{TiO}_2$  Nanocrystals: Comparison of Anatase, Rutile, and Brookite Polymorphs and Exploration of Surface Chemistry. *ACS Catal.* **2012**, *2*, 1817-1828.
- (45) Anpo, M.; Yamashita, H.; Ichihashi, Y.; Ehara, S. Photocatalytic Reduction of  $\text{CO}_2$  with  $\text{H}_2\text{O}$  on Various Titanium Oxide Catalysts. *J. Electroanal. Chem.* **1995**, *396*, 21-26.

**TOC Graphics:**

