

SCIENTIFIC REPORTS



OPEN

The Effect of Excess Electron and hole on CO₂ Adsorption and Activation on Rutile (110) surface

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Received: 13 January 2016

Accepted: 03 March 2016

Published: 17 March 2016

CO₂ capture and conversion into useful chemical fuel attracts great attention from many different fields. In the reduction process, excess electron is of key importance as it participates in the reaction, thus it is essential to know whether the excess electrons or holes affect the CO₂ conversion. Here, the first-principles calculations were carried out to explore the role of excess electron on adsorption and activation of CO₂ on rutile (110) surface. The calculated results demonstrate that CO₂ can be activated as CO₂ anions or CO₂ cation when the system contains excess electrons and holes. The electronic structure of the activated CO₂ is greatly changed, and the lowest unoccupied molecular orbital of CO₂ can be even lower than the conduction band minimum of TiO₂, which greatly facilitates the CO₂ reduction. Meanwhile, the dissociation process of CO₂ undergoes an activated CO₂⁻ anion in bent configuration rather than the linear, while the long crossing distance of proton transfer greatly hinders the photocatalytic reduction of CO₂ on the rutile (110) surface. These results show the importance of the excess electrons on the CO₂ reduction process.

The increasing industrial growth has led to accelerated energy consumption especially the traditional fossil fuel, which inevitable releases amount of CO₂ that results in seriously global warming problem. It is of great urgency to reduce CO₂ emission, and this problem is gaining plenty of attentions from various fields¹⁻³. In addition to the biological photosynthesis, different strategies such as physical and chemical approaches have been proposed to reduce and convert CO₂ to chemical fuels⁴⁻⁶. Photo-catalytic CO₂ conversion has been proved to be an efficient way to convert CO₂ by harnessing renewable solar energy, and it will generate synthetic fuels such as formaldehyde (HCHO), formic acid (HCOOH), methanol (CH₃OH), and methane (CH₄)⁷⁻⁹.

Titanium dioxide (TiO₂) is considered as a model photocatalysis for CO₂ conversion as it is highly stable, non-toxic and cheap^{10,11}. The early experiment proposed by Inoue *et al.*, reported that under UV light photo-catalytic reduction of CO₂ in the aqueous suspension of photosensitive semiconductor powders can form HCHO, HCOOH, CH₃OH, and CH₄ as main products⁷. Later, many efforts have been devoted to increase the efficiency and selectivity of the photo-catalytic CO₂ reduction¹²⁻¹⁶. The photo-catalytic CO₂ reduction results suggest that the catalytic activity can also be affected by TiO₂ phase, and they found that the brookite has a much higher activity than the anatase or rutile phase^{17,18}. Further, the efficiency and selectivity of CO₂ reduction can be improved through doping noble metals, such as Pt, Pd, Cu, and Au atoms on TiO₂¹⁹⁻²². A previous report showed that the efficiency of CO₂ conversion into fuels can also be significantly affected by the hole-sacrifice, such as methanol²³. Nonetheless, CO₂ can be successfully converted through photo-catalytic reduction, both the efficiency and selectivity of photo-catalytic system are still too low and poor for the realistic application. In order to design a more efficient and selective photo-catalyst, it is important to understand the detailed CO₂ reduction mechanism at the molecular level.

The photo-catalytic reduction of CO₂ into synthetic fuels is a multiple electron reaction process, which involves two-electron process to form CO and HCOOH, four-electron process to form HCHO, and eight-electron process to form CH₄^{3,24-26}. For all these multiple electron reaction processes, the process starts initially from the adsorption and activation of CO₂ molecule, in which CO₂ involves configuration transformation, such as linear CO₂ to bent and proton transfer takes place. In real reaction process, the activation of CO₂ is a rate-limiting step⁵. CO₂ is a rather inert molecule with a positive electron affinity of 0.6 ± 0.2 eV²⁷. Meanwhile, with respect to the normal hydrogen electrode (NHE), the reduction potential of CO₂/CO₂⁻ is about 1.9 eV, which is much higher

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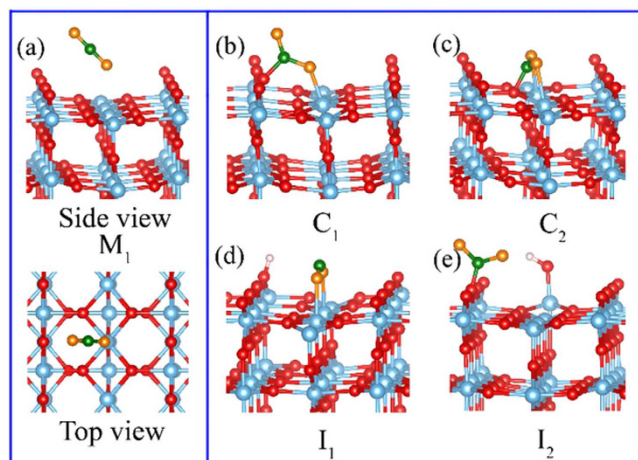


Figure 1. Different adsorption configurations of CO₂ adsorbed on excess electrons perfect rutile (110) surface. (a) M₁, molecular CO₂ adsorbs at five-fold Ti^{5f} in a tilted style. (b) C₁, one O atom of CO₂ bonds at the fivefold Ti^{5f}, and the C atom of CO₂ bonds with the bridge oxygen. (c) C₂, the two O atoms of CO₂ adsorb at two adjacent Ti^{5f} and the C atom bonding with the O^{3f} atom of TiO₂. (d) I₁, quite similar to C₂, while the C atoms does not interact with the surface oxygen atoms. (e) I₂, the C atom of CO₂ adsorbs on the top of the bridging oxygen in a tilted style. The O and Ti atoms in TiO₂ are represented in red and gray blue balls, while O and C atoms in CO₂ molecule are represented in orange and green balls.

than the TiO₂ conduction band minimum (CBM) about 0.4 eV above the Fermi level²⁸. Thus, such relatively high potential prevents the efficient electron transfer process from TiO₂ to CO₂, which is a necessary for the photo-catalytic reduction reaction.

On the other side, several experiments have shown that the CO₂ can be triggered on the pure TiO₂^{6,29}. The vibrational spectroscopic techniques have shown that CO₂⁻ anions is identified on pure TiO₂ surface, indicating electron can be transferred from TiO₂ to CO₂²³. Additionally, Tan *et al.* found that CO₂ molecule can be activated by one electron and reduced to CO on the reduced rutile (110) surface based on scanning tunneling microscopy³⁰. How to reconcile this paradox as most of the experimental results appear CO₂ can be converted, while lowest unoccupied molecular orbital (LUMO) value of CO₂ molecule is extremely high²⁸. On the theoretical side, He *et al.* reported the CO₂⁻ anion is one of the important species on the charged anatase (101) surface, and the reduction of CO₂ into HCOOH or CO mainly it takes 2e⁻ reaction on anatase TiO₂(101)^{31,32}. Thus, it is urgency to know how the excess electrons effect on the CO₂ adsorption and activation during the reduction process at the molecular level.

In this paper, we explore excess electrons effect on the structure and reactivity of CO₂ on the perfect and reduced rutile (110) by first-principles calculations. Spin moment and density calculations show that the CO₂ anion can exist in the TiO₂ (110) containing excess electrons, and a new configuration of CO₂ cation exists in the hole system. Furthermore, the electronic density of various CO₂ adsorptions show that the LUMO of CO₂ can be tuned by the excess electrons or hole. Especially, the LUMO of the activated CO₂ can even be lower than the TiO₂ CBM, which can effectively lower the reaction barrier. Our results show that the CO₂ activation and reduction processes on the rutile (110) surface are greatly affected by the excess electrons and holes.

Results

In the present study, we examine the effect of excess electrons on the CO₂ adsorption and activation on the perfect/reduced rutile (110) surfaces. We firstly focus on the role of excess electrons on the CO₂ adsorption configurations adsorbed on perfect rutile (110) surface. Later, intrinsic oxygen vacancy (O_v) defect is further explored. Further, we explore reaction pathway of CO₂ dissociation into CO on O_v rutile (110) surface and mechanism involves photo-catalytic reduction of CO₂ to form a HCOOH.

The excess electrons effect on CO₂ adsorption on the perfect rutile (110) surface. In this section, we initially focus on the possible CO₂ adsorption configurations in the case of excess electrons on the perfect rutile (110) surface. Before discussing the detailed CO₂ adsorption, it should be emphasized that the linear molecular CO₂ is firstly physically adsorbed on the rutile (110) surface. And according to the previous our results³³, the molecular CO₂ linearly adsorbed at five-fold Ti^{5f} in a tilted style is the most stable one. Based on this adsorption, the molecular CO₂ will undergo a translation into bend through activation or reduction. As a result, the molecular adsorbed CO₂ changes to the bend chemical adsorption. Five different binding configurations of CO₂ exist on rutile (110) surface. All possible adsorption configurations are examined, which are labeled as M₁, C₁, C₂, I₁ and I₂ (see Fig. 1). M₁ is a physical adsorption, where the CO₂ linearly adsorbs at five-fold Ti^{5f} in a tilted style. Except M₁, all other four C₁, C₂ and I₁, I₂ configurations are chemical adsorptions: In C₁ configuration, one O atom of CO₂ bonds to the fivefold Ti^{5f}, and the C atom of CO₂ interacts with the bridge oxygen, forming a bent CO₂ configuration; As for C₂, the two O atoms of CO₂ adsorbs at two adjacent Ti^{5f} sites, and the C atom directly bonds with the

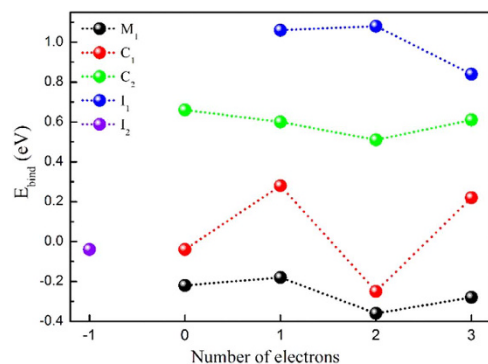


Figure 2. The binding energy of the CO₂ adsorptions vs the different number of excess electrons in perfect rutile (110) surface. The positive digit denotes the number of excess electrons, and the negative digit means the number of hole in the transverse axis. Here the negative value indicates relatively large adsorption energy.

Parameter	M ₁	C ₁	C ₂	I ₁	I ₂
Ti-O (Å)	2.60	1.94	2.16	2.13	
C-O (Å)	1.16	1.32	1.26	1.25	1.26
O-C-O (θ)	177.6	127.2	132.5	135.0	120.2
Net Charge (e)	0.05	-0.29	-0.29	-0.29	-0.05
Spin (μ _B)	0	0	0	0.74	0.90
Parameter	CO ₂	Ov-1	Ov-2	Ov-3	Ov-4
Ti-O (Å)		2.67	2.23	2.15	2.70
C-O (Å)	1.18	1.19	1.28	1.29	1.34
O-C-O (θ)	180.0	179.8	132.9	129.3	129.3
Net Charge (e)	0	0.06	-0.41	-0.43	-0.35
Spin (μ _B)	0	0	0.82	0	0
E _{bind} (eV)		-1.08	-0.16	-0.83	-1.11

Table 1. Representative geometrical parameters, net charge, spin polarized moment for the CO₂ adsorbed on excess electron perfect (M₁, C₁, C₂, I₁, and I₂) and reduce rutile (110) (O_{v-1}, O_{v-2}, O_{v-3}, and O_{v-4}) surface. The binding energy for CO₂ on reduced TiO₂ is also included.

O^{3f} atom of TiO₂; Quite similar to C₂, the C atom of I₁ does not interact with surface oxygen atom; As for I₂, the CO₂ adsorbs on the top of the bridging oxygen, forming a new C-O^{2f} bond.

In Fig. 2, the positive digit in the transverse axis represents the number of excess electron, while the negative digit denotes the number of hole. When the system does not contain any excess electron or hole, three different binding configurations of CO₂ on the perfect TiO₂ were identified after the geometry relaxation, namely M₁, C₁ and C₂. The others, I₁ and I₂, are unstable. The corresponding binding energy shows that M₁ has the largest binding energy of -0.23 eV as the system does not contain excess electron, which is a little smaller than the earlier reported pure PBE value of -0.35 eV^{33,34}. This is because PBE+U functional treats the d-orbital of Ti in a more localization.

As an electron is introduced to TiO₂, I₁ can exist with a binding energy of 1.02 eV. Therefore, the CO₂ adsorption in I₁ is meta-stable. It should be noted that the same kind configuration is also reported on the anatase (101) surface, and the corresponding adsorption energy of CO₂ is 0.78 eV³¹, which is quite close the current one. When more electrons are included in TiO₂, no new configuration appears, and the corresponding binding energy are also not sensitive to the number of excess electrons. When the TiO₂ surface is charged with holes, the configuration of I₂ can exist with a binding energy of -0.05 eV.

The detailed geometrical parameters, net charge, and spin polarized moment of the CO₂ adsorption configurations are also calculated as shown in Table 1. Among these five states, the configurations of M₁, C₁ and C₂ adsorbed on the perfect without excess electron or hole are chosen as they are not sensitive to the excess electrons. While the configurations of I₁ and I₂ are shown for the system containing one electron or hole. Compared with the single CO₂ molecule, the C-O bond length of CO₂ in M₁ is almost similar, and the ∠O-C-O angle slightly decreases by 2.38°. The net charge and spin polarized moment of adsorbed CO₂ are the same to that of single CO₂ molecule. A keen look into the structures of the C₁/C₂, the C-O bond length in C₁/C₂ increases by 0.08/0.14 Å, while the ∠O-C-O bond angle decreases by 53.76/47.45°. In case of C₁ and C₂, owing to the strong interaction between the CO₂ and rutile (110) surface, charge transfer occurs from TiO₂ to CO₂ by about 0.29e⁻. The spin polarized moment of these two adsorbed CO₂ states is zero, demonstrating that there is no unpaired electron existing in both C₁ and C₂.

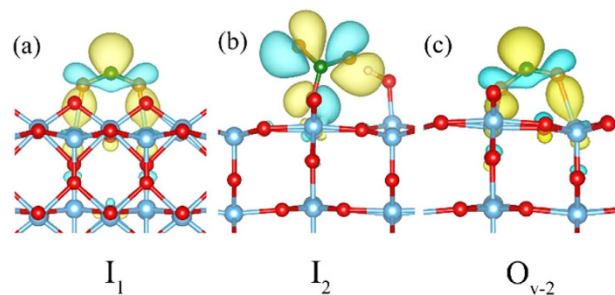


Figure 3. Spin densities of different binding configurations of CO₂ on excess electrons perfect and O_v rutile (110) surface. Spin density of (a) I₁ with an excess electron and (b) I₂ with a hole on the perfect rutile (110) surface. (c) spin density of O_{v-2} on the reduced rutile (110) surface.

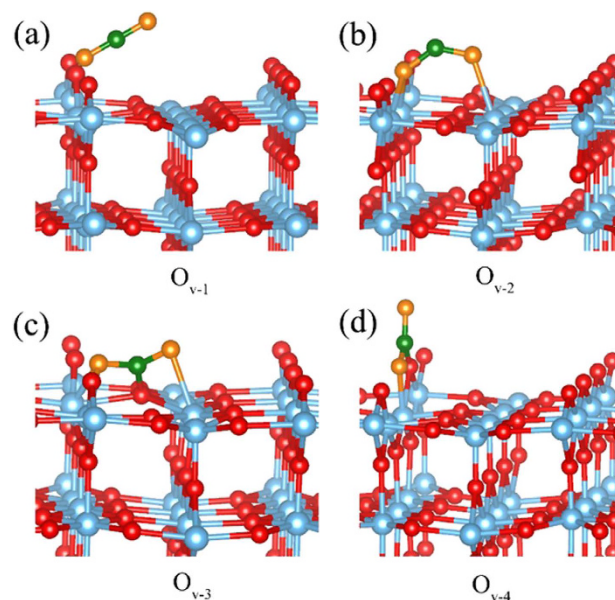


Figure 4. Different adsorption configurations of CO₂ on O_v rutile (110) surface. (a) O_{v-1}, CO₂ molecule adsorbed at O_v site in a tilted style. (b) O_{v-2}, one O of CO₂ adsorbed at O_v site and the other O adsorbed at Ti^{5f} in the plane. (c) O_{v-3}, quite similar to O_{v-2} except for the C atom linked to O^{3f} in the plane. (d) O_{v-4}, one O atom of CO₂ adsorbed at O_v site and the C atom adsorbed with the O^{2f} near the O_v site.

As we mentioned above, when the system contains the excess electron, the I₁ becomes metastable. As for the I₁, the relaxed geometric parameters (Ti-O, C-O and ∠O-C-O) of I₁ and net charges are quite close to C₂, but the spin polarized moment is 0.74 μ_B, indicating an unpaired electron is located on the CO₂ forming an activated state of I₁. The corresponding spin densities as shown in Fig. 3. The excess electron is mainly localized on the C atom of the CO₂, suggesting that an excess electron is transferred from TiO₂ to CO₂ and to form a CO₂⁻ anion³¹. It should be mentioned that although this configuration is rather unfavorable, the extra electron is shown to be critical to stabilize this binding configuration. When it comes to I₂, the C-O bond length is little elongated to 1.27 Å, and the ∠O-C-O angle enormously decreases to 120.27°. The spin polarized moment is about 0.90 μ_B, indicating an unpaired electron is located on CO₂. Further spin density calculation demonstrates that the electron in I₂ is localized at the two O atoms instead of C atom in the CO₂ forming an activated CO₂⁺ cation as shown in Fig. 3, which is different from the previous reported result only forming CO₂⁻ state³¹. From the above results, we clearly observe that various CO₂ adsorptions appear on the perfect rutile (110) surface in the case of excess electrons or holes.

CO₂ adsorption on O_v rutile (110) surface. Apart from excess electron on the perfect TiO₂ case, the intrinsic oxygen vacancy (O_v) defect can also provide two excess electrons to the rutile TiO₂(110)³⁵. Here, we consider one O_v defect in rutile (110) surface to simulate the effect of excess electrons on the CO₂ adsorption. Relative to the above perfect TiO₂, O_v defect not only provides the excess electrons but also the adsorption sites.

Here, four different configurations are examined, labeled as O_{v-1} ~ O_{v-4} as shown in Fig. 4. O_{v-1} linearly adsorbs in the middle of O_v in a tilted configuration. In case of O_{v-2}, one of the O atom of CO₂ binds to two 5-fold Ti atoms (Ti^{5f}) in the O_v site through bi-dentate fashion, while the other “O” atom interacts with the 5-fold Ti atom (Ti^{5f}) in the plane. The configuration of O_{v-3} is quite close to O_{v-2} except for the C atom linked to the 3-fold “O” atom (O^{3f})

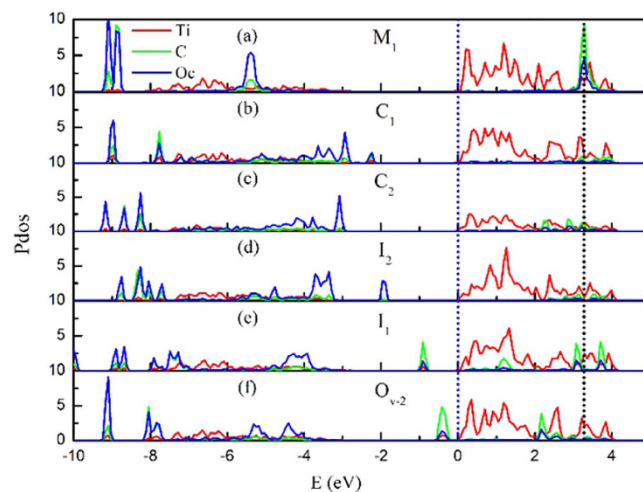


Figure 5. The partial density of states (PDOS) of the different CO₂ adsorption configurations on the excess electrons rutile (110) surface. (a) PDOS for the molecular CO₂ adsorption state M₁, and (b)/(c) corresponds to bending adsorption state C₁/C₂. (d,e) PDOS for I₂ with an hole and I₁ with an excess electron, respectively. (f) PDOS for O_{v-2} adsorbed on reduced rutile (110). The plots in red is the PDOS of the single Ti atom adsorbed by the CO₂. The plots in green and blue are the C atom and O atom of the adsorbed CO₂, respectively.

in the plane; the CO₂ in O_{v-4} adsorbs in the bridging oxygen row with the O mono-dentate adsorbed to Ti^{5f} in O_v site and C atom bonds to bridging oxygen O^{2f}.

The corresponding binding energies, geometrical parameters, net charge, and spin polarized moment of the CO₂ adsorption on reduced TiO₂ are also summarized in Table 1. Previous theoretical result shows that the CO₂ interacting with O_{v-4} configuration on the anatase (101) cluster is the most stable adsorption with the binding energy of -1.09 eV³¹. Similarly, the calculated binding energy of CO₂ in O_{v-4} has the highest binding energy of -1.11 eV in our present study, indicates that O_{v-4} is indeed more favorable adsorption. The binding energy of O_{v-1} is about -1.08 eV, which is quite close to O_{v-4} suggesting that O_{v-1} is also relatively stable configuration. The other two configurations O_{v-2} and O_{v-3} have relatively lower binding energies than O_{v-1} and O_{v-4}, indicating that they are meta-stable.

A keen look into the geometrical parameters of O_{v-1}~O_{v-4}, the CO₂ in O_{v-1} configuration both bond lengths and angles are very close to the isolated CO₂ molecule (Table 1). Unlike the O_{v-1}, the bond length of C-O in O_{v-2}~O_{v-4} is elongated by 0.1–0.16 Å, and the angle ∠O-C-O significantly decreases by 47.05–50.68° compared with an isolated CO₂ molecule. Similar to C₁ and C₂ on perfect TiO₂ (110), net charge of O_{v-2}~O_{v-4} is about $-0.41e^-$, suggesting that charge redistribution between CO₂ and TiO₂. Most strikingly, spin polarized moment studies shows that the O_{v-1}, O_{v-3}, and O_{v-4} the calculated spin moments are equal to zero, whereas O_{v-2} has a spin moment of 0.82 μ_B, indicating an electron is located in the CO₂. Further spin density calculation reveals that the electron is localized on the C atom of the CO₂ as shown in Fig. 3. Thus, the CO₂ in O_{v-2} indeed converts into an activated CO₂⁻ anion. Although O_{v-2} has a relatively lower binding energy than other configurations, the extra electron at “C” atom is crucial to stabilize the binding configuration.

It is well known that the LUMO value of an isolated CO₂ molecule is very high, and the electron is very difficult to transfer to the CO₂ molecule from the TiO₂ conduction band³. In order to know whether the above CO₂ adsorptions can affect the LUMO of CO₂ in the presence of excess electron or hole, the partial density of states (PDOS) of the adsorbed CO₂ is calculated. The results are shown in Fig. 5. As for M₁, the LUMO value is located above the TiO₂ CBM onset by 3.4 eV. This value is in consistent with the estimated value of 3.5 eV by Indrakanti *et al.*, and a little larger than the value of 2.3 eV by Tan *et al.*^{3,30}. Thus, the electron in the TiO₂ CBM is rather difficult to be transferred to the CO₂ in molecular state. When the CO₂ is changed to bending adsorption configurations (C₁ and C₂), the localized LUMO of CO₂ molecule becomes delocalized state, and the LUMO onset shifts down to 2.3 eV. Therefore, the energy level can be modified by CO₂ adsorption mode. Whereas this value is still too large for the electron transfer from the TiO₂ conduction band to the CO₂ molecule. When the CO₂ adsorptions with the configurations of I₁, I₂, and O_{v-2} on TiO₂ (110) containing excess electron or hole, the PDOS shows the LUMO of CO₂ shifts further downward, which can even be lower than the TiO₂ CBM. Hence, the electron or hole can easily transfer from TiO₂ CBM to the CO₂ with I₁, I₂, and O_{v-2}.

Dissociation of CO₂ into CO on O_v rutile (110) surface. As discussed above, the CO₂ adsorption on the O_v rutile (110) surface can be activated, and the corresponding LUMO is even lower than TiO₂ CBM. Thus it is interesting to know how the CO₂ adsorption on O_v rutile (110) can be further converted into the other species. The activation process can be expressed as:



From the equation (2), we can clearly observe that the activation of CO₂ process needs an excess electron in the system. Scanning tunneling microscopy experiment suggested that the conversion of CO₂ to CO is relative to

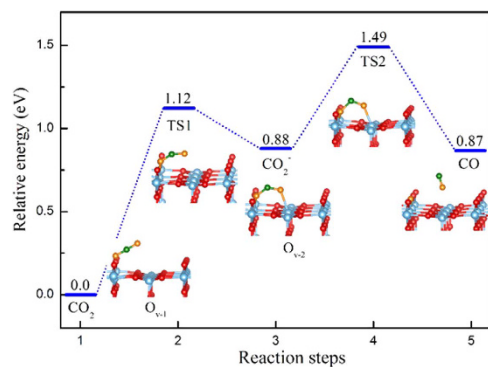


Figure 6. Illustration of reaction pathway via O_{v-2} configuration to form CO. The sum energy of the CO_2 and O_v rutile TiO_2 is the zero reference for energy.

electron attachment state of linear CO_2 molecule on the O_v rutile (110) surface³⁰. However, the detailed dissociation of CO_2 mechanism at molecular level is still unknown. Here, we start the study from configuration O_{v-1} with intrinsic excess electrons in reduced TiO_2 , and the dissociation of CO_2 into CO are explored. The detailed reaction pathway and calculated energy barriers are shown in Fig. 6.

As shown in Fig. 6, the CO_2 molecule firstly adsorbs at the oxygen vacancy, forming the linear adsorption as O_{v-1} . In this step, there is no electron transfer from reduced TiO_2 to linear CO_2 , which is a different from the previous result where the linear CO_2 can form an electron attachment state³⁶. Then, the linear adsorbed CO_2 molecule initiates to bent, which undergoes a transition state transition state 1 (TS1) with an energy barrier 1.12 eV to form O_{v-2} structure. Subsequently, the excess electron in the TiO_2 transfers to the CO_2 , forming CO_2^- anion (see Fig. 3). On the basis of CO_2^- anion, the C-O bond breaks to form CO, leaving an O atom at the oxygen vacancy site. The energy barrier of this process is about 0.61 eV. From the whole process, the CO formation undergoes an activation state of O_{v-2} rather than a direct C-O bond breaking of linear CO_2 .

Photo-catalytic reduction of CO_2 to form HCOOH. Apart from the CO formation in the reduced TiO_2 , photo-catalytic reduction of CO_2 can also form synthetic fuels such as formaldehyde (HCHO), formic acid (HCOOH), methanol (CH_3OH), and methane (CH_4) on the TiO_2 based materials. However, the formation of these useful fuels through activated CO_2 is still rare, and most of the theoretical researches mainly focus on the anatase phase³². Here, on the basis of configuration I_1 , the reduction of CO_2 to form HCOOH is investigated, which can be expressed as:



From equations (3) to (5), we can clearly understand that the reaction involves two electrons and two protons in the system. The complete reduction process can be divided into five steps as follows: The molecular CO_2 firstly adsorbs on the rutile (110) surface as C_1 ; Following this, excess electron injects into CO_2 , and the corresponding CO_2 becomes CO_2^- anion as I_1 ; Then, one proton and electron transfer to the CO_2^- anion, forming HCO_2^- ; Finally, the other proton transfers to HCO_2^- , forming HCOOH.

According to the above reaction processes, the transition states and corresponding energy barriers of CO_2 reduction to HCOOH are summarized in Fig. 7. On the basis of configuration C_1 , the two O atoms of CO_2 begin to bend towards the adjacent fivefold Ti^{5f} in plane through TS1, the two O atoms of CO_2 is adsorbed by Ti^{5f} in nature as shown step-3 in Fig. 7. Consecutively, the electron spontaneously transfers to the CO_2 forming the CO_2^- anion. This process needs to overcome an energy barrier of 1.28 eV, which is much higher than the case in anatase (101) of 0.87 eV³². Consecutive proton and electron move to the "C" atom of CO_2^- anion to form HCO_2^- . These findings are very different from the case in anatase (101). In anatase case, proton transfer occurs with no energy barrier, but the proton transfer on rutile needs to overcome an energy barrier of 0.93 eV. The calculated energy barrier is relatively higher, because the proton should move about 3.10 Å between the adsorbed proton and the CO_2^- anion, which is larger than the one in anatase (about 2.60 Å). Further, the other proton moves to the "O" atom of HCO_2^- , resulting in HCOOH. This process needs a moderate energy barrier of 0.75 eV. From the complete reduction process, the formation of CO_2^- anion is the rate limiting step, and also the proton transfer step is much difficult than the earlier reported anatase (101) surface³².

Activation of CO_2 by a hole. On the basis of configuration I_2 , the activation of CO_2 by the hole is also investigated, which can be expressed as:



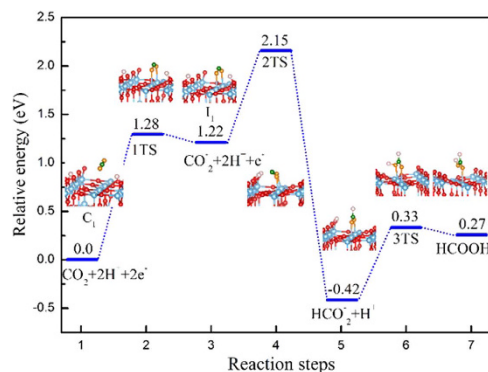


Figure 7. Illustration of reaction pathway via I_1 configuration to form HCOOH. The sum of energies of the CO_2 and 2H is the zero reference for energy. The sign of “+” indicates non-interacting species (e.g. $\text{CO}_2 + \text{OH}$), and the transition state denotes by TS.

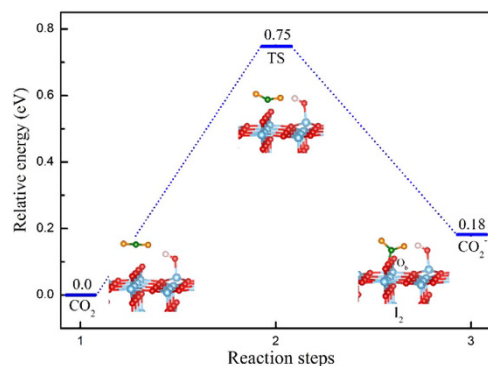


Figure 8. Illustration of reaction pathway to form CO_2^+ cation. The sum energy of CO_2 and TiO_2 is set to zero as the reference energy.

In the CO_2 activation process (Eq. 6), a hole is transferred to the O atom of CO_2 in configuration I_2 . The detailed reaction process and activation barrier of hole to CO_2 with I_2 are calculated (Fig. 8). The molecular CO_2 adsorbs on the top of bridge oxygen on TiO_2 with a C-O_b distance of 2.71 Å. Then the C atom of the CO_2 moves towards the bridge-site oxygen. In the transition state geometry, the C-O_b distance decreases from 2.71 Å to 1.74 Å. Finally, the “C” atom of CO_2 adsorbed with the bridge oxygen forming a bent like CO_2 , and the C-O_b distance decreases to 1.34 Å. Simultaneously, the hole is transferred to the two “O” atoms of CO_2 forming a CO_2^+ as shown in Fig. 3. Formation of cation need to overcome a relatively lower energy barrier (about 0.75 eV) than that of anions.

Discussions

In summary, by the first-principles calculations, structural and reactivity behavior of CO_2 on rutile TiO_2 are greatly affected by excess electrons. The computed results show that various CO_2 adsorption configurations appear in the case of excess electrons, and activated CO_2 adsorption configurations can be exist in the not only excess electron system as I_1 and O_{v-2} , but also in the hole system as I_2 . Further electronic density calculation shows that the LUMO of CO_2 can be modified by varying the CO_2 adsorption states, and it can even be lowered and below the TiO_2 conduction band. The detailed CO_2 activation and reduction processes are also explored. The mechanism of CO_2 reduction to CO on oxygen vacancy rutile (110) surface is revised, the reduction process involves the formation of CO_2 anion in bend type structure with an energy barrier of 1.12 eV. The results also suggest that, the energy barrier of rate limitation step to form HCOOH is about 1.28 eV. In addition, the process for the formation of CO_2^+ cation in the hole system is also investigated, and it needs a much lower energy barrier of 0.75 eV.

Method

The calculations are performed based on the spin-polarized density functional theory (DFT) in periodic boundary conditions, as implemented in the CP2K/Quickstep package³⁷. This simulation code employs hybrid Gaussian and plane wave (GPW) basis sets and norm conserving Goedecker-Teter-Hutter (GTH) pseudo-potentials to represent the ion-electron interactions^{38,39}. The Gaussian functions consisting of a double- ζ plus polarization (DZVP) basis set was employed to optimize the structures⁴⁰. The energy cutoff for the real space grid was 500 Ry, which yields total energies converged to at least 0.001 eV per atom. For the exchange-correlation functional, we have used the Perdew-Burke-Ernzerhof (PBE) functional of generalized gradient approximation (GGA)⁴¹. The

vdW correction is considered with the Grimme approach (DFT-D3)⁴². Since the standard GGA functional has the limitation to calculate the d-band electrons of transition metal, GGA+U functional is used to treat Ti 3d electron with $U = 4.2 \text{ eV}$ ⁴³. In order to avoid the interaction between the adjacent images, a vacuum spacing of 15 \AA is employed for all the systems. Transition states along the reaction pathways are searched by the Climbing Image Nudged Elastic Band (CI-NEB) approach⁴⁴.

The interaction between the adsorbed molecule and the substrate, which can be characterized by the binding energy, which is defined as,

$$E_b = E_{\text{ab/sub}} - E_{\text{ad}} - E_{\text{sub}} \quad (6)$$

where $E_{\text{ad/sub}}$ is the total energy of the molecule adsorbed on the substrate, E_{ad} is the energy of the isolated molecule in the same box, and the E_{sub} is the energy of the substrate. In the present study, a (4×2) supercell is used to represent rutile TiO_2 (110) substrate containing four tri-layers. In the rutile TiO_2 (110) features three types of under coordinated atoms: five-fold Ti ionic (Ti^{5f}), bridge oxygen atom in two-fold (O^{2f}), and planar three-fold oxygen atom (O^{3f}). The excess electrons in the system are simulated by adding hydrogen atoms or hydroxyls, and one hydrogen/hydroxyl corresponds to one electron/hole⁴⁵. All the CO_2 adsorption configurations studied in the text, only one CO_2 molecule is considered to adsorb on the (4×2) supercell, corresponding to $1/8 \text{ ML}$ coverage.

References

- Tu, W., Zhou, Y. & Zou, Z. Photocatalytic Conversion of CO_2 into Renewable Hydrocarbon Fuels: State-of-the-Art Accomplishment, Challenges, and Prospects. *Adv Mater* **26**, 4607–4626, doi: 10.1002/adma.201400087 (2014).
- Dhakshinamoorthy, A., Navalon, S., Corma, A. & Garcia, H. Photocatalytic CO_2 reduction by TiO_2 and related titanium containing solids. *Energ Environ Sci* **5**, 9217–9233, doi: 10.1039/c2ee21948d (2012).
- Indrakanti, V. P., Kubicki, J. D. & Schobert, H. H. Photoinduced activation of CO_2 on Ti-based heterogeneous catalysts: Current state, chemical physics-based insights and outlook. *Energ Environ Sci* **2**, 745–758, doi: 10.1039/b822176f (2009).
- Liu, L. J. & Li, Y. Understanding the Reaction Mechanism of Photocatalytic Reduction of CO_2 with H_2O on TiO_2 -Based Photocatalysts: A Review. *Aerosol Air Qual Res* **14**, 453–469, doi: 10.4209/aaqr.2013.06.0186 (2014).
- Burghaus, U. Surface chemistry of CO_2 – Adsorption of carbon dioxide on clean surfaces at ultrahigh vacuum. *Prog. Surf. Sci.* **89**, 161–217, doi: 10.1016/j.progsurf.2014.03.002 (2014).
- Krischok, S., Hoff, O. & Kempter, V. The chemisorption of H_2O and CO_2 on TiO_2 surfaces: studies with MIES and UPS (HeI/II). *Surf. Sci.* **507**, 69–73, doi: 10.1016/S0039-6028(02)01177-9 (2002).
- Inoue, T., Fujishima, A., Konishi, S. & Honda, K. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature* **277**, 637–638, doi: 10.1038/277637a0 (1977).
- Dimitrijevic, N. M. *et al.* Role of water and carbonates in photocatalytic transformation of CO_2 to CH_4 on titania. *J. Am. Chem. Soc.* **133**, 3964–3971, doi: 10.1021/ja108791u (2011).
- Yu, J., Low, J., Xiao, W., Zhou, P. & Jaroniec, M. Enhanced Photocatalytic CO_2 -Reduction Activity of Anatase TiO_2 by Coexposed {001} and {101} Facets. *J. Am. Chem. Soc.* **136**, 8839–8842, doi: 10.1021/ja5044787 (2014).
- Schneider, J. *et al.* Understanding TiO_2 photocatalysis: mechanisms and materials. *Chem. Rev.* **114**, 9919–9986, doi: 10.1021/cr5001892 (2014).
- Ma, Y., Wang, X., Chen, X., Han, H. & Li, C. Titanium Dioxide-Based Nanomaterials for Photocatalytic Fuel Generations. *Chem. Rev.* **114**, 9987–10043, doi: 10.1021/cr500008u (2014).
- Henderson, M. A. Evidence for bicarbonate formation on vacuum annealed TiO_2 (110) resulting from a precursor-mediated interaction between CO_2 and H_2O . *Surf. Sci.* **400**, 203–219, doi: 10.1016/S0039-6028(97)00863-7 (1997).
- Lo, C. C., Hung, C. H., Yuan, C. S. & Wu, J. F. Photoreduction of carbon dioxide with H_2 and H_2O over TiO_2 and ZrO_2 in a circulated photocatalytic reactor. *Sol Energy Mat Sol C* **91**, 1765–1774, doi: 10.1016/j.solmat.2007.06.003 (2007).
- Varghese, O. K., Paulose, M., LaTempa, T. J. & Grimes, C. A. High-Rate Solar Photocatalytic Conversion of CO_2 and Water apor to Hydrocarbon Fuels. *Nano letters* **9**, 731–737, doi: 10.1021/nl803258p (2008).
- Indrakanti, V. P., Kubicki, J. D. & Schobert, H. H. Quantum Chemical Modeling of Ground States of CO_2 Chemisorbed on Anatase (001), (101), and (010) TiO_2 Surfaces. *Energ Fuel* **22**, 2611–2618, doi: 10.1021/ef700725u (2008).
- Roy, S. C., Varghese, O. K., Paulose, M. & Grimes, C. A. Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons. *ACS Nano* **4**, 1259–1278, doi: 10.1021/nn9015423 (2010).
- Liu, L., Zhao, H., Andino, J. M. & Li, Y. Photocatalytic CO_2 Reduction with H_2O on TiO_2 Nanocrystals: comparison of Anatase, Rutile, and Brookite Polymorphs and Exploration of Surface Chemistry. *ACS Catal.* **2**, 1817–1828, doi: 10.1021/cs300273q (2012).
- Rodriguez, M. M., Peng, X., Liu, L., Li, Y. & Andino, J. M. A Density Functional Theory and Experimental Study of CO_2 Interaction with Brookite TiO_2 . *J. Phys. Chem. C* **116**, 19755–19764, doi: 10.1021/jp302342t (2012).
- Yui, T. *et al.* Photochemical reduction of CO_2 using TiO_2 : effects of organic adsorbates on TiO_2 and deposition of Pd onto TiO_2 . *ACS Appl. Mater. Interfaces* **3**, 2594–2600, doi: 10.1021/am200425y (2011).
- Yamashita, H., Nishiguchi, H., Kamada, N. & Anpo, M. Photocatalytic Reduction Of CO_2 With H_2O On TiO_2 And Cu/TiO_2 Catalysts. *Res. Chem. Intermed* **20**, 815–823, doi: 10.1163/156856794X00568 (1994).
- Sen, S., Liu, D. & Palmore, G. T. R. Electrochemical Reduction of CO_2 at Copper Nanofoams. *ACS Catal.* **4**, 3091–3095, doi: 10.1021/cs500522g (2014).
- Xie, S., Wang, Y., Zhang, Q., Fan, W. & Deng, W. Photocatalytic reduction of CO_2 with H_2O : significant enhancement of the activity of Pt- TiO_2 in CH_4 formation by addition of MgO. *Chem. Commun.* **49**, 2451–2453, doi: 10.1039/c3cc00107e (2013).
- Ulagappan, N. & Frei, H. Mechanistic Study of CO_2 Photoreduction in Ti Silicalite Molecular Sieve by FT-IR Spectroscopy. *J. Phys. Chem. A* **104**, 7834–7839, doi: 10.1021/jp001470i (2000).
- Mori, K., Yamashita, H. & Anpo, M. Photocatalytic reduction of CO_2 with H_2O on various titanium oxide photocatalysts. *RSC Adv.* **2**, 3165, doi: 10.1039/c2ra01332k (2012).
- Lee, J., Sorescu, D. C. & Deng, X. Electron-induced dissociation of CO_2 on TiO_2 (110). *J. Am. Chem. Soc.* **133**, 10066–10069, doi: 10.1021/ja204077e (2011).
- Pipornpong, W., Wanbayor, R. & Ruangpornvisuti, V. Adsorption CO_2 on the perfect and oxygen vacancy defect surfaces of anatase TiO_2 and its photocatalytic mechanism of conversion to CO. *Appl. Surf. Sci.* **257**, 10322–10328, doi: 10.1016/j.apsusc.2011.06.013 (2011).
- Sommerfeld, T., Meyer, H. D. & Cederbaum, L. S. Potential energy surface of the CO_2^- anion. *Phys. Chem. Chem. Phys.* **6**, 42–45, doi: 10.1039/b312005h (2004).
- Indrakanti, V. P., Schobert, H. H. & Kubicki, J. D. Quantum Mechanical Modeling of CO_2 Interactions with Irradiated Stoichiometric and Oxygen-Deficient Anatase TiO_2 Surfaces: Implications for the Photocatalytic Reduction of CO_2 . *Energ Fuel* **23**, 5247–5256, doi: 10.1021/ef9003957 (2009).

29. Acharya, D. P., Camillone, N. & Sutter, P. CO₂ Adsorption, Diffusion, and Electron-Induced Chemistry on Rutile TiO₂(110): A Low-Temperature Scanning Tunneling Microscopy Study. *J. Phys. Chem. C* **115**, 12095–12105, doi: 10.1021/jp202476v (2011).
30. Tan, S. *et al.* CO₂ dissociation activated through electron attachment on the reduced rutile TiO₂(110)-1 × 1 surface. *Phys. Rev. B* **84**, 155418(1)-155418(5), doi: 10.1103/PhysRevB.84.155418 (2011).
31. He, H. Y., Zapol, P. & Curtiss, L. A. A Theoretical Study of CO₂ Anions on Anatase (101) Surface. *J. Phys. Chem. C* **114**, 21474–21481, doi: 10.1021/jp106579b (2010).
32. He, H., Zapol, P. & Curtiss, L. A. Computational screening of dopants for photocatalytic two-electron reduction of CO₂ on anatase (101) surfaces. *Energ Environ Sci* **5**, 6196–6205, doi: 10.1039/c2ee02665a/ (2012).
33. Yin, W. J., Krack, M., Wen, B., Ma, S. & Liu, L. CO₂ Capture and Conversion on Rutile TiO₂(110) in the Water Environment: Insight by First-Principles Calculations. *J. Phys. Chem. Lett.* **2538–2545**, doi: 10.1021/acs.jpcclett.5b00798 (2015).
34. Sorescu, D. C., Lee, J., Al-Saidi, W. A. & Jordan, K. D. Coadsorption properties of CO₂ and H₂O on TiO₂ rutile (110): a dispersion-corrected DFT study. *J. Chem. Phys.* **137**, 074704(1)-074704(16), doi: 10.1063/1.4739088 (2012).
35. Sun, C., Liu, L. M., Selloni, A., Lu, G. & Smith, S. C. Titania-water interactions: a review of theoretical studies. *J. Mater. Chem.* **20**, 10319, doi: 10.1039/c0jm01491e (2010).
36. Tan, S. *et al.* CO₂ dissociation activated through electron attachment on the reduced rutile TiO₂(110)-1 × 1 surface. *Phys. Rev. B* **84**, 155418(1)-155418(5), doi: 10.1103/PhysRevB.84.155418 (2011).
37. Vondele, V. *et al.* Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Commun.* **167**, 103–128, <http://dx.doi.org/10.1016/j.cpc.2004.12.014> (2005).
38. Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* **54**, 1703–1710, <http://dx.doi.org/10.1103/PhysRevB.54.1703> (1996).
39. Krack, M. Pseudopotentials for H to Kr optimized for gradient-corrected exchange-correlation functionals. *Theor Chem Acc* **114**, 145–152, doi: 10.1007/s00214-005-0655-y (2005).
40. VandeVondele, J. & Hutter, J. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J. Chem. Phys.* **127**, 114105(1)-114105(9), doi: 10.1063/1.2770708 (2007).
41. Perdew, J., Burke, K. & Matthias, H. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868, <http://dx.doi.org/10.1103/PhysRevLett.77.3865> (1996).
42. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104(1)-154104(19), doi: 10.1063/1.3382344 (2010).
43. Ji, Y., Wang, B. & Luo, Y. Location of Trapped Hole on Rutile-TiO₂(110) Surface and Its Role in Water Oxidation. *J. Phys. Chem. C* **116**, 7863–7866, doi: 10.1021/jp300753f (2012).
44. Henkelman, Uberuaga, G., Jónsson, B. P. & Hanne, A. climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **113**, 9901–9904, <http://dx.doi.org/10.1063/1.1329672> (2000).
45. Di Valentin, C., Pacchioni, G. & Selloni, A. Electronic Structure of Defect States in Hydroxylated and Reduced Rutile TiO₂(110) Surfaces. *Phys. Rev. Lett.* **97**, 166803(1)-166803(4), doi: 10.1103/PhysRevLett.97.166803 (2006).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 51572016, 51222212). This research work is supported by a Tianhe-2JK computing time award at the Beijing Computational Science Research Center (CSRC). Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (the second phase).

Author Contributions

The idea was conceived by L.L. The simulation was performed by W.Y. The data analyses were performed by W.Y., B.W., S.B., M.K., M.L. and L.L. This manuscript was written by W.Y. and L.L. All authors discussed the results and contributed to the paper.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Yin, W.-J. *et al.* The Effect of Excess Electron and hole on CO₂ Adsorption and Activation on Rutile (110) surface. *Sci. Rep.* **6**, 23298; doi: 10.1038/srep23298 (2016).



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