Effect of Bimetallic Dimer-Embedded TiO$_2$(101) Surface on CO$_2$ Reduction: The First-Principles Calculation

Chongyang Li $^{1,2,*}$, Cui Shang $^3$, Bin Zhao $^{4,*}$, Gang Zhang $^1$, Liangliang Liu $^{5,*}$, Wentao Yang $^4$ and Zhiquan Chen $^{2,*}$

$^1$ College of Electric Power, North China University of Water Resources and Electric Power, Zhengzhou 450045, China; lichongyang@ncwu.edu.cn (C.L.); zg15937100954@163.com (G.Z.)
$^2$ Henan Key Laboratory of Magnetoelectronic Information Functional Materials, School of Physics and Electronics Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, China; sc906@zzuli.edu.cn
$^3$ Henan Key Laboratory of Magnetoelectronic Information Functional Materials, School of Physics and Electronics Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, China; zhouko2008@163.com
$^4$ School of Science, Zhongyuan University of Technology, Zhengzhou 450007, China; liull@henu.edu.cn (L.L.); chenzq@whu.edu.cn (Z.C.)
$^*$ Correspondence: zhaobin@zut.edu.cn (B.Z.); liull@henu.edu.cn (L.L.); chenzq@whu.edu.cn (Z.C.)

1. Introduction

Global warming is a serious challenge for human activity today; it is also a global environmental issue recognized by the international community [1,2]. The main reason for global warming is the results of the rise in global population [3–5], solid wastes [6], as well as the correspondingly dramatic and continuing uptrend in the concentration of greenhouse gases worldwide, of which carbon dioxide (CO$_2$) is the largest contributor [7]. Three kinds of CO$_2$-conversion strategies exist: electrocatalysis, thermal-catalysis, and photocatalysis, to the direct conversion of CO$_2$ into valuable fuel and chemical products under ambient conditions [8–11], which has attracted increasing attention from researchers [12–16]. However, the CO$_2$-reduction reaction (CO$_2$RR) still suffers from low faradaic efficiency, low conversion efficiency, sluggish kinetics of the primary side reaction of hydrogen-evolution reaction, and high overpotential, which have greatly hindered its further practical applications. Based on this, transition-metal (TM)-based catalysts have been applied to improve the CO$_2$RR performance [17], as well as waste-originated biorenewables and other catalysts [18–22].
The well-noted single-atom catalyst (SAC) was first attempted to design and synthesize novel materials by defect, modification, high-temperature shockwave, and self-assembly, which have enabled various catalytic conversions, including CO$_2$RR with extremely higher atom efficiency, activity, and durability [23–27]. Double-atom catalysts (DACs) such as Cu-Pt [28–31], Cu-Au [32–34], and Pd-Au [35] in many mainstream reactions have also been experimented, characterized, and developed to improve CO$_2$-reduction-reaction efficiency, offering a fascinating catalyst model for theorists to explore, and hence gaining enormous attention. DACs usually exhibit better catalytic performance than SACs [28,34,35]. This is mainly due to their tuning diversity and synergistic effect between adjacent active sites of metal dimers, resulting in low-coordination metal atoms and an extra metal site. The interaction of different metal sites could accelerate the intrinsic CO$_2$RR performance of bimetallic dimer-embedded catalysts. For example, Baldovi et al. [34] loaded Au-, Cu-, and Au/Cu-alloy NPs on the surface of TiO$_2$. The study showed that the introduction of Cu into Au/Cu-TiO$_2$ could boost the transfer of the CB electrons in TiO$_2$ to CO$_2$, resulting in a higher conversion efficiency toward CO$_2$ reduction to CH$_4$. Zheng et al. [35] introduced a secondary metal (Au) to support the Pd catalyst, and Au concentration could alter the dominant reaction pathway, which was much more favorable for CO$_2$ reduction performance. Therefore, the combination of non-noble metals and noble metals and even the non-noble metal dimers embedded on TiO$_2$ substrate might be a novel and effective method to promote CO$_2$ adsorption and conversion.

Meanwhile, many studies [36–39] found that CO was an important intermediate in the transformation of CH$_4$, CH$_3$OH, and HCHO. The CO$_2$-reduction reaction can be regarded as a “series reaction”. CO$_2$ molecules need to be converted into CO first to obtain the target gas product. Therefore, it is a feasible strategy to design bimetallic dimer TiO$_2$ catalysts that can firmly adsorb CO to achieve CO$_2$ reduction to CH$_4$.

Based on the first-principles calculation, we explored CO$_2$ reduction on TiO$_2$ with M-N (M, N = Cu, Pt, Zn) dimer doping. We mainly calculated both the binding energy and charge distributions of the bimetallic dimer-embedded A-TiO$_2$(101) substrate and the CO$_2$ molecule adsorbed on these dimer-embedded A-TiO$_2$(101) catalysts, respectively. We also calculated the Bader charge and Charge Density Difference (CDD) from the TiO$_2$ substrate to the bimetallic dimer and from the bimetallic dimer-embedded TiO$_2$ to CO$_2$ gas molecule. The results indicated that the structure of the bimetallic dimer-embedded TiO$_2$(101) surface was stable, and the CO$_2$ molecule could stably stay on the bimetallic dimer-embedded TiO$_2$(101) surface. Then, the CO$_2$ reduction reactivity was proposed. The energy barrier of the Zn-Cu dimer-embedded TiO$_2$(101) surface was as low as 0.31 eV, which was a much more suitable choice as well as advantageous in terms of economy. Therefore, the findings of this study might theoretically provide an effective strategy for the designing of effective CO$_2$-reduction TiO$_2$-based catalysts.

2. Computational Details

Based on the density functional theory, all first-principles calculations were used in the CO$_2$ adsorption and reduction on the bimetallic dimer-embedded A-TiO$_2$(101) surface. Projected augmented-wave pseudopotentials, generalized-gradient-approximation (GGA) method [40–42], and Perdew–Burke–Ernzerhof (PBE) functional were employed using Vienna Ab-initio Simulation Package (VASP, vasp.5.4.1, Hafner team of University of Vienna, Vienna, Austria) [43–45] through the computational simulations. For the kinetic processes, the previous studies indicated that the GGA-PBE approach could correctly describe CO-oxidation, CO$_2$-dissociation, and O-diffusion [46,47] reaction paths on the surface. The cutoff of the kinetic energy for the plane wave was set to be 450 eV. Further, $2 \times 2 \times 1$ was used for the Monkhorst-Pack k-point mesh during geometry optimizations, and the corresponding electronic structure calculations were set as $3 \times 3 \times 1$. The convergence criterion for the electronic was chosen as $10^{-3}$ eV, and the maximum force of each atom for ionic relaxation was 0.02 eV/Å. Regarding the dissociation and diffusion of the CO$_2$ reduction process, the transition state (TS) search was performed by the climbing-image
nudged-elastic-band method [48–50]. Bader charge analysis was used to obtain the electronic transformation, and charge-density difference was calculated to observe its charge distribution [51].

The lattice parameters of the A-TiO$_2$ system were $a = 3.830$ Å and $c = 9.613$ Å. A $3 \times 2$ surface supercell of TiO$_2$ with three stoichiometric (TiO$_2$)-structure layers was selected, of which the bottom TiO$_2$ layer was fixed to simulate the bulk structure and the total atom was 108, to investigate the CO$_2$ adsorption and dissociation performance. In the direction perpendicular to the (101) plane, the thickness of the vacuum layer was set to be 10 Å to eliminate the influence between the adjacent layers.

When Zn-Cu, Zn-Pt, and Cu-Pt dimers were embedded onto the surface of TiO$_2$(101), the binding energy ($E_b$) of this bimetallic dimer-embedded A-TiO$_2$(101) substrate was defined as

$$E_b = E_{\text{surface+dimer}} - E_{\text{surface}} - E_{\text{TiO}_2}$$

where $E_{\text{surface+dimer}}$ is the system energy of the bimetallic dimer-embedded TiO$_2$; $E_{\text{surface}}$ is the system energy without bimetallic dimer; and $E_{\text{dimer}}$ is the energy of independent bimetallic dimer.

To explore the adsorption performance of CO$_2$ molecules on a bimetallic dimer-embedded A-TiO$_2$(101) surface, the adsorption energy ($E_{\text{CO}_2\text{ad}}$) was defined as

$$E_{\text{CO}_2\text{ad}} = E_{\text{surf+CO}_2} - E_{\text{surf}} - E_{\text{CO}_2}$$

where $E_{\text{surf+CO}_2}$ is the system energy of adsorbed CO$_2$ molecules on a bimetallic dimer-embedded A-TiO$_2$(101) surface; $E_{\text{surf}}$ is the system energy without the adsorbed CO$_2$ molecule; $E_{\text{CO}_2}$ is the energy of the free gas molecules.

3. Results and Discussions

3.1. Bimetallic Sites on Anatase TiO$_2$(101) Surface

We chose three bimetallic combinations, Zn-Cu, Zn-Pt, and Cu-Pt, to observe the CO$_2$ adsorption and reduction on a bimetallic dimer-embedded TiO$_2$(101) surface. If a bimetallic dimer was embedded on the A-TiO$_2$(101) surface, several possible binding sites could be selected. We chose the most suitable embedded sites through serval configurations of metal-embedded A-TiO$_2$(101), which are shown in Figure 1. The binding energy of Zn-Cu, Zn-Pt, and Cu-Pt on the surface of A-TiO$_2$(101) was $\approx 2.34$ eV, $\approx 3.6$ eV, and $\approx 2.9$ eV, respectively, indicating that bimetallic-dimer interstitials could stably stay on the A-TiO$_2$(101) surface, along with bond length of M-N, M-O$_{2c}$, N-Ti and the angle of O$_{2c}$-M-O$_{2c}$, as listed in Table 1.

![Figure 1](image-url)
Zn-Pt, and Cu-Pt interstitials of the TiO\(_2\) (101) surface from a side view, respectively. The isosurface value was set as 0.0025 e/bohr\(^3\). The electron accumulation is denoted with the yellow regions; green indicates electron depletion. The Cu atom in dark blue color, Pt atom is pale, and Zn atom in light gray color.

**Table 1.** Calculated results for bimetal-embedded A-TiO\(_2\) systems, including the distance \(d_{M-N}\) between two metal atoms; \(d_{M-O}\) and \(d_{M-N}\) is the distance of metal M and O\(_{\text{Ti}}\), and Ti and metal N atom, respectively. The angle of O\(_{\text{O2c}}\)-M-O\(_{\text{O2c}}\) is equal to \(\angle O_{\text{O2c}}\)-M-O\(_{\text{O2c}}\). The binding energies of bimetallic atoms on A-TiO\(_2\)(101) (\(E_b\)) and the charge transfer from A-TiO\(_2\) to bimetallic atoms (\(\Delta Q\)). M stands for the former metal atom, and N stands for the later one.

| Dimer     | \(d_{M-N}\) (Å) | \(d_{M-O}\) (Å) | \(\angle O_{\text{O2c}}\)-M-O\(_{\text{O2c}}\) (°) | \(d_{\text{Ti-N}}\) (Å) | \(E_b\) (eV) | \(\Delta Q\) (e) |
|-----------|-----------------|----------------|-----------------------------------|-----------------|-------------|-------------|
| Zn-Cu     | 2.32            | 2.07           | 108.42°                           | 2.62            | −2.34       | −0.85       |
| Zn-Pt     | 2.39            | 2.02           | 114.96°                           | 2.28            | −3.60       | −0.52       |
| Cu-Pt     | 2.48            | 1.92           | 135.90°                           | 2.29            | −2.90       | −0.60       |

Bader charge analysis and CDD were also performed to further study the stability of the bimetallic dimer-embedded TiO\(_2\) surface. As listed in Table 1, about 0.85 e, 0.52 e, and 0.60 e were transferred from the embedded Zn-Cu, Zn-Pt, and Cu-Pt dimers to the A-TiO\(_2\)(101) substrate for these three different configurations (Figure 1), respectively, which were mainly accepted by the neighboring O atoms. The interaction between embedded bimetallic dimers and A-TiO\(_2\)(101) surface led to the charge redistribution and the accumulation of electrons around the Zn-O, Zn-O, Cu-Pt bonds for Zn-Cu, Zn-Pt, and Cu-Pt dimer embedded TiO\(_2\) systems, respectively, which could be confirmed by CDD as shown in Figure 1d–f. Further, the partial density of states (PDOS) of three dimer-TiO\(_2\)(101) systems, as shown in Figure 2, revealed many impurity peaks induced by 2p orbital electrons of O atom and 3d orbital electrons of Zn and Cu atoms, indicating that the chemical activity of embedded TiO\(_2\) surface was relatively stronger. Therefore, the results of PDOS, Bader charge analysis, and CDD demonstrated the formation of strong chemical bonds between Zn-Cu, Zn-Pt, Cu-Pt dimers and neighboring oxygen atoms. Therefore, the A-TiO\(_2\)(101) surface embedded with Zn-Cu, Zn-Pt, and Cu-Pt dimers were chemically stable.

### 3.2. One CO\(_2\) Molecule Adsorbed on the Bimetal-TiO\(_2\)(101) Surface

When a CO\(_2\) molecule came close to these three configuration surfaces, it will be adsorbed on the surface. Before further exploring the CO\(_2\) adsorption and reduction on the bimetal-TiO\(_2\)(101) surface, several adsorbed sites were determined, and the most stable surface models for Zn-Cu, Zn-Pt, and Cu-Pt dimers were obtained, as shown in Figure 3. For these three configurations, the adsorption energies for CO\(_2\) molecules of −0.15 eV, −0.17 eV, and −0.13 eV, respectively. The calculation results demonstrated weaker physical adsorption between the CO\(_2\) molecule and bimetallic interstitial. The structure of CO\(_2\) molecule is nearly the same with the gas state with the bond length of 1.18 Å and \(\angle O_{(1)}\)-C-O\(_{(2)}\) around 180°. At the same time, the results of the charge transfer from A-TiO\(_2\) to the bimetallic dimer showed few electrons transferring from the CO\(_2\) molecules to the dimer-embedded TiO\(_2\) substrate, namely 0.03 e, 0.02 e, and 0.02 e for Zn-Cu, Zn-Pt, and Cu-Pt dimer-embedded TiO\(_2\)(101) systems, respectively. Thus, the interactions between the CO\(_2\) molecule and the dimer-embedded A-TiO\(_2\)(101) surface were relatively weaker. All these results showed a weaker physical absorption between the system and CO\(_2\) molecules.
Meanwhile, the CO\textsubscript{2} gas molecule was more stably adsorbed onto the bimetal-embedded TiO\textsubscript{2} surface with a small barrier energy, which was about 0.03 eV, 0.23 eV, and 0.12 eV for the Zn-Cu, Zn-Pt, and Cu-Pt series, respectively. The final stable adsorbed structures are shown in Figure 4a–c. Moreover, the charge distribution from CDD is shown in Figure 4d–f. As shown in Figure 4, the CO\textsubscript{2} molecules were bound to the dimer-TiO\textsubscript{2}(101) system via the bimetallic atoms. The distances between the C atom and the nearest embedded metal of the dimer-TiO\textsubscript{2} substrate were shortened to be 1.87 Å, 2.00 Å, and 1.99 Å for Zn-Cu, Zn-Pt, and Cu-Pt adsorption cases, respectively, which were much nearer than those of the initial adsorption cases. Moreover, the bonds of O(1)–C and C-O(2) were enlarged to be about 1.24 Å and 1.30 Å, respectively, and the adsorption energies were elevated up to −0.36 eV, −0.46 eV, and −0.97 eV for Zn-Cu, Zn-Pt, and Cu-Pt cases, respectively. Therefore,
the adsorption of CO₂ molecules on the dimer-TiO₂(101) surface should be a chemical adsorption behavior.

| Zn-Cu side view | Zn-Pt side view | Cu-Pt side view |
|------------------|------------------|------------------|
| (a) | (b) | (c) |

| Charge distribution | Charge distribution | Charge distribution |
|---------------------|---------------------|---------------------|
| (d) | (e) | (f) |

Figure 4. Most stable configurations (a–c) and the corresponding charge-density differences (d–f) of a CO₂ molecule absorbed on the Zn-Cu, Zn-Pt, and Cu-Pt dimer-embedded A-TiO₂(101) surface from a side view. The isosurface value was set as 0.0025 e/bohr³. The electron accumulation is denoted with the yellow regions, while the electron depletion is denoted with green regions. The Cu atom in dark blue color, Pt atom is pale, and Zn atom in light gray.

The partial densities of states of the absorbed CO₂ on the bimetallic dimer-embedded TiO₂ system (bimetallic dimers were Zn-Cu, Zn-Pt, and Cu-Pt) were calculated to further understand this adsorption performance, which are shown in Figure 5. When CO₂ molecules were adsorbed on the bimetal-embedded TiO₂ surface, we could clearly observe the hybridization with the orbitals of adsorbed CO₂ molecules and 3d orbitals of dopant Zn, Cu, and Pt atoms, implying the formation of Zn-O, Cu-O, and Pt-O bonds on the interface between the adsorbed CO₂ molecules and the dimer-TiO₂ system. Moreover, the Bader charge analysis revealed about 0.82 e, 0.67 e, and 0.54 e transferred from the CO₂ molecules to the dimer-embedded TiO₂ substrate for Zn-Cu, Zn-Pt, and Cu-Pt dimers (see Table 2). In addition to the calculations of charge distribution, we could see that the accumulation of charge occurred around metal-O bonds; the CDD is plotted in Figure 4d–f. The results of the charge transfer and charge redistribution demonstrated the strong chemical interaction between the dopant dimer of Zn-Cu, Zn-Pt, and Cu-Pt and nearby O adatoms, namely Zn-O, Zn-O, and Cu-O bonds. This might be the reason for the increase in O₁-C and C-O₂ bond lengths. Further, we found that the adsorption energy of the Cu-Pt-TiO₂ system was relatively higher, which was two times more than that of other two cases. The absolute value of charge transfer for the Zn-Cu-TiO₂ system, as well as the extents of overlap of electronic states was also larger. Therefore, the aforementioned results, especially the structural variation and charge redistribution of CO₂ molecules and different dimer-TiO₂ substrates, showed stronger chemical interaction between CO₂ molecules and dimer-embedded TiO₂(101) surface. Thus, CO₂ molecules could stably stay and were chemically adsorbed. The details of initial physical adsorption to final chemical adsorption, along with the reduction process, were as follows.
Table 2. Calculated results for a CO₂ molecule on an A-TiO₂(101) surface during the adsorption process. d_{M,N} and d_{O(1)} are the bond lengths between metal M and metal N, and between the O(1) atom and the C atom, respectively, for chemical adsorption structure. E_{CO2ads} stands for the adsorption energy of CO₂ adsorbed on TiO₂(101) surface. ΔQ is the charge transfer from bimetallic dimer-embedded TiO₂ to CO₂ molecule. M stands for the former metal atom, and N stands for the latter one.

|        | d_{M-N} (Å) | d_{M-O(1)} (Å) | d_{O(1)-C} (Å) | θ_{O₂c-M-O₂c} (°) | d_{C-N} (Å) | d_{O₂-N} (Å) | E_{CO2ads} (eV) | ΔQ (e) |
|--------|-------------|----------------|----------------|------------------|-------------|-------------|----------------|-------|
| Pure TiO₂ | -           | -              | 1.18           | 1.18             | -           | -           | -0.31          | -     |
| Zn-Cu   | 3.45        | 1.90           | 1.24           | 1.30             | 125.92      | 1.87        | 1.90           | -0.36 | 0.82 |
| Zn-Pt   | 2.68        | 1.97           | 1.24           | 1.29             | 130.90      | 1.99        | 2.25           | -0.46 | 0.67 |
| Cu-Pt   | 2.63        | 1.90           | 1.23           | 1.30             | 132.32      | 1.99        | 2.52           | -0.97 | 0.54 |

3.3. CO₂ Reduction on the Zn-Cu, Zn-Pt, and Cu-Pt Dimer-Embedded Anatase TiO₂(101) Surface

After determining the structure and CO₂ adsorption of bimetallic dimer-embedded on the A-TiO₂(101) surface, we first discussed the effect of the Zn-Cu dimer-embedded A-TiO₂(101) substrate on the reduction of the CO₂ molecule. We chose the direct reduction pathway. We determined the optimized structures of the TSs across dissociation and diffusion processes, as well as the products involved in this pathway, which are shown in Figure 6. For the Zn-Cu-CO₂ system, CO₂ molecules subsequently dissociated into the adsorbed "CO of the O-C-Cu bond and "O" bonded with Cu, Zn, and Ti atoms onto the surface via the transition states TS1, TS2, and TS3 and intermediate states A2 and A3. The asterisk (*) is denoted as the adsorbed sites. When a CO₂ molecule was adsorbed on the surface of the Zn-Cu dimer-embedded A-TiO₂(101) surface, the Cu and Zn atoms could diffuse to adsorb the CO₂ molecule and the Zn-Cu bond was broken, which resulted in...
the formation of new bonds of Cu-O(1), Cu-C, Cu-Ti, and Zn-O(2). The energy barrier for TS1 was only 0.03 eV, and then the CO₂ molecule could be stably adsorbed onto the surface of the TiO₂ system.

As shown in Figure 6b, A2 was the initial configuration and the CO₂ gas phase dissociated. A lower energy of 0.31 eV was needed for the dissociation step. In this step, the O(1) atom diffused away and led to the breaking of the Cu-O(1) bond, while the O(2) atom moved a little nearer and then bonded with Cu, Zn, and Ti atoms, which were much closer to the A-TiO₂(101) surface through TS2. With a decrease of 0.84 eV, the Zn-Cu-TiO₂(101) system achieved a more stable structure than A2 after this transformation. However, A3 was a metastable configuration, since C and O(2) from the gas phase exhibited more polarity. The interaction with the surface Cu atom was enhanced, and the more active atom of embedded Cu easily diffused outward to be adsorbed by OC* to a more stable site by an energetic driving force. With a tiny energy barrier of 0.17 eV, the diffusion of A3 transforming into A4 was achieved easily. As a result, with the breaking of the Cu-Ti bond, the new bonds of O(1)-C, C-Cu, and Cu-O(2) were aligned in a straight line with the bond lengths of 1.15 Å, 1.76 Å, and 1.79 Å. For the whole reaction process of A1 → A2 → A3 → A4 (Figure 6), the highest-energy barrier and the total reaction energy of CO₂ reduction on the Zn-Cu-TiO₂ system were 0.31 eV and 0.72 eV, respectively, corresponding to the transformation from A2 to A4. The results indicated that the reaction of CO₂ dissociation became much easier...
with the help of the Zn-Cu dimer embedded on the A-TiO$_2$(101) surface. The embedded dimer might also contribute a more active site on the surface and improve the CO$_2$ reduction behaviors. Meanwhile, the configuration structure also became more stable upon CO$_2$ adsorption and reduction reaction on the dimer-embedded A-TiO$_2$ surface.

After a CO$_2$ molecule was adsorbed on the A-TiO$_2$(101) surface, the structure B1 was first obtained easily without nearly any difference with the independent CO$_2$ gas phase and the Zn-Pt-TiO$_2$ system, as shown in Figure 1b, indicating the physical adsorption of the stable structure B1. For the structure B1, the embedded Zn and Pt atoms were particularly prone to adsorb CO$_2$ molecules. Then, a much more stable structure B2 was obtained through TS4 with an energy barrier of 0.23 eV (Figure 7a); the system energy slightly decreased by 0.28 eV. As a result, the two new bonds of Pt-C and Zn-O (2) were formed, and the adsorption energy of the CO$_2$ molecule increased to $-0.46$ eV. The adsorbed CO$_2$ molecule on the surface became much more stable via chemical adsorption. For B2 as the initial configuration, the adsorbed CO$_2$ molecule was dissociated on the Zn-Pt dimer-embedded TiO$_2$(101) surface, as shown in Figure 7b. The dissociation energy barrier of the adsorbed CO$_2$ molecule was 1.69 eV, which was much higher than that in the Zn-Cu case, as shown in Figure 6b. In the transition state TS5, the adsorbed CO$_2$ molecule was dissociated, along with the breaking of C-O (2) and Pt-Ti bonds and the formation of new bonds of Pt-O (2) and Pt-O$_3$ on the subsurface. For the whole reaction path of C1 $\rightarrow$ TS4 $\rightarrow$ C2 $\rightarrow$ TS5 $\rightarrow$ C3, the highest-energy barrier was 1.69 eV, and the system energy decreased by 0.9 eV. The results also demonstrated that the dissociated CO was stably adsorbed on the Zn-Pt dimer-embedded TiO$_2$(101) surface, and the final structure B3 also became much more stable.

For the Cu-Pt case, the structures C1 and C4 were initial and final configurations; the dissociation-reaction energy and energy barrier were $-1.34$ eV and 1.58 eV, respectively. Similarly to the former two dimer-embedded TiO$_2$(101) surfaces, a more stable structure, C2, was obtained with a lower-energy barrier of 0.12 eV. Obviously, the new Pt-C and Cu-O (2) chemical bonds of 1.99 Å and 1.90 Å, were formed. The C-O (2) bond was strengthened to be 1.30 Å with a small bend of CO$_2$ molecules, while the Cu-Pt bond was broken. Subsequently, the adsorbed CO$_2$ molecule began to dissociate, as shown in Figure 8b. In the transition state TS7, the C-O (2) bond of the CO$_2$ molecule was initially broken, with a dissociation-energy barrier of 1.58 eV. As a result, O (2) atoms moved nearer to the TiO$_2$(101) surface, and a relatively more stable structure C3 was obtained, along with the formation of new bonds of O (2)-Cu, O (2)-Pt, and O (2)-Ti. At the same time, C3 was a metastable configuration. The Pt atom could easily move out to be grabbed by the *CO adatom during TS7 and TS8 with the distance varying from 1.99 Å, 1.85 Å to 1.82 Å via an energetic driving force. Via the diffusion of TS8, the embedded Pt atom of structure C4 was more attracted to the *CO adatom with exothermic energy and energy barrier of 0.18 eV and 0.7 eV, respectively. For the C1 $\rightarrow$ C2 $\rightarrow$ C3 $\rightarrow$ C4 reaction path (Figure 8), the highest dissociation energy barrier was 1.59 eV, between those of TS5 and TS2 (TS2: 0.31 and TS5: 1.69 eV, respectively). The total energy of structure C4 was reduced by 1.34 eV, which was much higher than that of the two former systems. It showed that with the help of Cu-Pt dimer atoms, the dissociation process of CO$_2$ on the A-TiO$_2$(101) surface also required a relatively high-energy barrier.

We studied the adsorption and reduction performance of CO$_2$ molecules on three configurations of bimetallic dimer-embedded TiO$_2$(101): Zn-Cu, Zn-Pt, and Cu-Pt. We found unpaired electrons induced by the transfer of the bimetallic dimer to the O atom of the TiO$_2$ substrate. While a CO$_2$ molecule appeared on the TiO$_2$(101) surface, a partial excess charge of the bimetallic dimer was used to absorb the CO$_2$ gas molecule. However, the adsorption energy was relatively low, indicating only weaker physical adsorption. The final product was mainly CO, with the O atom bonded with the surrounding metal atom due to the CO$_2$-dissociation process on the bimetallic dimer-embedded TiO$_2$(101) surface.
Figure 7. CO$_2$ reduction on Zn-Pt-embedded A-TiO$_2$(101) surface. The Cu atom in dark blue, Pt atom is pale, and Zn atom in light gray. (a) is the adsorption process, and (b) is the reduction process.

For the CO$_2$ reduction process on the Zn-Cu-embedded TiO$_2$(101) surface, the highest-energy barrier was as low as 0.31 eV with the breaking of the C-O$_{\text{2}}$ bond and the formation of Cu-O$_{\text{2}}$, Zn-O$_{\text{2}}$, and Ti-O$_{\text{2}}$ bonds, which was relatively suitable to produce CO and O adatoms easily. However, relatively higher-energy barriers existed for Zn-Pt and Cu-Pt dimer-embedded TiO$_2$(101) systems, namely 1.69 eV and 1.58 eV, respectively. As shown in Figures 7b and 8b, the C-O$_{\text{2}}$ bonds of these two systems were also broken, besides the formation of three metal-O$_{\text{2}}$ bonds. However, the Zn-Pt-TiO$_2$ system had higher reaction energy of 0.62 eV, promoting thermal-catalytic performance. With lower barrier energy of 0.31 eV, the Zn-Cu dimer-embedded TiO$_2$(101) surface might be a much more convenient design for the CO$_2$RR of the bimetallic dimer-embedded TiO$_2$ substrate, as well as a more economical method compared with noble metals such as Pt, Au, and Ag. Therefore, the findings of this study might theoretically provide an effective strategy for the designing of effective CO$_2$-reduction TiO$_2$-based catalysts.
The adsorption energy of CO molecules and the bimetallic dimer-embedded TiO$_2$ surface had the values of 0.31 eV, 1.69 eV, and 1.58 eV, respectively, which benefited the reduction process. Furthermore, the surface-electronic states also implied stronger interaction between CO molecules and the bimetallic dimer-embedded TiO$_2$ surface. Moreover, the Bader charge analysis exhibited only 0.03 e transferring from the dimer to the adsorbent atoms, confirming the stronger interaction. Regarding the CO$_2$ dissociation process, the results showed that the dissociation barriers of the CO$_2$ molecule with Zn-Cu, Zn-Pt, and Cu-Pt dimers embedded on the TiO$_2$(101) surface had the values of 0.31 eV, 1.69 eV, and 1.58 eV, respectively, which benefited the CO$_2$-reduction reaction (CO$_2$RR) activity. Meanwhile, it was observed that the products *CO and *O* of CO$_2$ reduction were firmly adsorbed on the dimer-embedded TiO$_2$(101) surface. In addition, the bonds of metal-O(2)-metal were less than 2.00 Å, and metal-C and C-O(1) bonds were relatively shortened to be 1.76 Å and 1.15 Å, respectively. From the viewpoint of the activation barrier and reaction energy, the Zn-Cu dimer-embedded...
TiO$_2$(101) substrate was more favorable for CO$_2$ direct reduction than the other two kinds of bimetallic dimer-embedded TiO$_2$(101) surfaces. Meanwhile, compared with partial noble atoms such as Pt, Au, and Ag, the combination of Zn and Cu atoms was a much more suitable choice, as well as being advantageous in terms of economy with the energy barrier of 0.31 eV. Therefore, our study theoretically provided a new design of the high CO$_2$RR performance of Zn-Cu dimer-embedded A-TiO$_2$ substrate catalysts.

**Author Contributions:** Writing—original draft preparation, C.L.; writing—review and editing, C.L.; software, C.S.; First-Principles calculation, L.L. and B.Z.; data curation, G.Z.; picture processing, W.Y.; general guidance, Z.C. All authors have read and agreed to the published version of the manuscript.

**Funding:** This project was supported by the National Natural Science Foundation of China (Grant Nos. 11805295 and 11804311), the key scientific and technological project of Henan Province (Grant Nos. 212102210490, 222102230087) and the funding scheme for young backbone teachers of Zhongyuan University of Technology (Grant No. 2018XQG17).

**Institutional Review Board Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available within the article.

**Conflicts of Interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**References**

1. USDC. *Trends in Atmospheric Carbon Dioxide, Monthly AverAge Mauna Loa CO$_2*$ National Oceanic and Atmospheric Administration: Silver Spring, MD, USA; Earth System Research Laboratory: Boulder, CO, USA; Global Monitoring Division: Boulder, CO, USA; United States Department of Commerce: Washington, DC, USA, 2021. Available online: https://gml.noaa.gov/ccgg/trends/ (accessed on 17 July 2021).

2. Manojkumar, N.; Srimuruganandam, B. Size-segregated particulate matter and health effects in air pollution in India: A review. *Environ. Chem. Lett.* 2021, 19, 3837–3858. [CrossRef]  

3. Desa, U. *World Population Prospects 2019: Highlights*; United Nations Department for Economic and Social Affairs: New York, NY, USA, 2019.

4. Millati, R.C.; Ariyanto, T.; Azzahrani, I.N.; Putri, R.U.; Taherzadeh, M.J. *Sustainable Resource Recovery and Zero Waste Approaches*; Elsevier: New York, NY, USA, 2019.

5. Khanal, S.K.; Varjani, S.; Lin, C.S.K.; Awasthii, M.K. Waste-to-resources: Opportunities and challenges. *Bioresour. Technol.* 2020, 317, 23987. [CrossRef][PubMed]

6. Abdel-Shafy, H.I.; Mansour, M.S.M. Solid waste issue: Sources, composition, disposal, recycling, and valorization. *Egypt J. Petrol.* 2018, 27, 1275–1290. [CrossRef]  

7. Hussain, M.; Liu, G.; Yousaf, B.; Ahmed, R.; Uzma, F.; Ali, M.U.; Ullah, H.; Butt, A.R. Regional and sectoral assessment on climate-change in Pakistan: Social norms and indigenous perceptions on climate-change adaptation and mitigation in relation to global context. *J. Clean. Prod.* 2018, 200, 791–808. [CrossRef]

8. Mustafà, A.; Lougou, B.G.; Shuai, Y.; Wang, Z.; Tan, H. Current technology development for CO$_2$ utilization into solar fuels and chemicals: A review. *J. Energy Chem.* 2020, 49, 96–123. [CrossRef]

9. Tackett, B.M.; Gomez, E.; Chen, J.G. Net reduction of CO$_2$ via its thermocatalytic and electrocatalytic transformation reactions in standard and hybrid processes. *Nat. Catal.* 2019, 2, 381–386. [CrossRef]  

10. Huang, B.; Wu, Y.; Luo, Y.; Zhou, N. Double atom-anchored Defective Boron Nitride catalyst for efficient electroreduction of CO$_2$ to CH$_4$: A first principles study. *Chem. Phys. Lett.* 2020, 756, 137852. [CrossRef]

11. Liu, Z.; Sun, Z. Reductive Transformation of Carbon Dioxide. *Acta Phys. Chim. Sin.* 2021, 37, 2012024. [CrossRef]

12. Gao, D.; Zhang, Y.; Zhou, Z.; Cai, F.; Zhao, X.; Huang, W.; Li, Y.; Zhu, J.; Liu, P.; Yang, F.; et al. Enhancing CO$_2$ Electroreduction with the Metal–Oxide Interface. *J. Am. Chem. Soc.* 2017, 139, 5652–5655. [CrossRef]

13. Kim, D.; Resasco, J.; Yu, Y.; Asiri, A.M.; Yang, P. Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold–copper bimetallic nanoparticles. *Nat. Commun.* 2014, 5, 4948. [CrossRef]

14. Liu, C.; Yang, B.; Tyo, E.; Seifert, S.; DeBartolo, J.; von Issendorff, B.; Zapol, P.; Vajda, S.; Curtiss, L.A. Carbon Dioxide Conversion to Methanol over Size-Selected Cu$_2$ Clusters at Low Pressures. *J. Am. Chem. Soc.* 2015, 137, 8676–8679. [CrossRef][PubMed]

15. Bai, S.; Shao, Q.; Wang, P.; Dai, Q.; Wang, X.; Huang, X. Highly Active and Selective Hydrogenation of CO$_2$ to Ethanol by Ordered Pd–Cu Nanoparticles. *J. Am. Chem. Soc.* 2017, 139, 6827–6830. [CrossRef]

16. Lakshmidevi, J.; Ramesh Naidu, B.; Venkateswarlu, K. A rapid-room temperature synthesis of α-cyanoacrylates, α-cyanoacrylonitriles and 4H-pyrans using water extract of pomegranate ash as catalytic media. *Sustain. Chem. Pharm.* 2022, 25, 100610. [CrossRef]
17. Wang, Z.; Hong, J.; Ng, S.-F.; Liu, W.; Huang, J.; Chen, P.; Ong, W.-J. Recent Progress of Perovskite Oxide in Emerging Photocatalysis Landscape: Water Splitting, CO₂ Reduction, and N₂ Fixation. *Acta Phys. Chim. Sin.* **2020**, *37*, 2011033. [CrossRef]

18. Naidu, B.R.; Lakshmidevi, J.; Naik, B.S.S.; Venkateswarlu, K. Water extract of pomegranate ash as waste-originated biorenewable catalyst for the novel synthesis of chiral tert-butanesulfinyl aldehydes in water. *Mol. Catal.* **2021**, *511*, 111719. [CrossRef]

19. Appa, R.M.; Naidu, B.R.; Venkateswarlu, D.; Hanafi, M.M.; Lakkaboyana, S.K.; Lakshmidevi, J.; Venkateswarlu, K. Water extract of pomegranate ash—I2 as sustainable system for external oxidant/metal/catalyst-free oxidative iodonation of (hetero)arenes. *Green Chem.* *Lett. Rev.* **2021**, *14*, 700–712. [CrossRef]

20. Di Giovannantonio, M.; Kosmala, T.; Bonanni, B.; Serrano, G.; Zema, N.; Turchini, S.; Catone, D.; Wandelt, K.; Pasini, D.; Contini, G.; et al. Surface-Enhanced Polymerization via Schiff-Base Coupling at the Solid–Water Interface under pH Control. *J. Phys. Chem. C* **2015**, *119*, 19228–19235. [CrossRef]

21. Di Giovannantonio, M.; El Garah, M.; Lipton-Duffin, J.; Meunier, V.; Cardenas, L.; Revurat, Y.F.; Cossaro, A.; Verdini, A.; Perpechika, D.F.; Rosei, F.; et al. Insight into Organometallic Intermediate and Its Evolution to Covalent Bonding in Surface-Confinmed Ullmann Polymerization. *ACS Nano* **2013**, *7*, 8190–8198. [CrossRef]

22. Kloppe, J.M.; Pasini, D.; Byers, J.D.; Willson, C.G.; Frechet, J.M.J. Microlithographic assessment of a novel family of transparent and etch-resistant chemically amplified 193-nm resists eased on cyclopolymercs. *Chem. Mater.* **2001**, *13*, 4147–4153. [CrossRef]

23. Lakshmidevi, J.; Vakati, V.; Naidu, B.R.; Raghavender, M.; Rao, K.S.V.K.; Venkateswarlu, K. Pd(5%)-KIT-6, Pd(5%)-SBA-15 and Pd(5%)-SBA-16 catalysts in water extract of pomegranate ash: A case study in heterogenization of Suzuki-Miyaura reaction under external base and ligand free conditions. *Sustain. Chem. Pharm.* **2021**, *19*, 100371. [CrossRef]

24. Zhou, X. TiO₂ Supported Single-Atom Catalysts for Photocatalytic Reactions. *Acta Phys. Chim. Sin.* **2020**, *37*, 2008064. [CrossRef]

25. Cai, S.; Wang, L.; Heng, S.; Li, H.; Bai, Y.; Dang, D.; Wang, Q.; Zhang, P.; He, C. Interaction of Single-Atom Platinum–Oxygen Vacancy Defects for the Boosted Photodegradation of H₂ Evolution and CO₂ Reduction: Experimental and Theoretical Study. *J. Phys. Chem. C* **2020**, *124*, 24566–24579. [CrossRef]

26. Huang, L.; Li, W.; Zeng, M.; He, G.; Shearing, P.R.; Parkin, I.P.; Lee, D.J.L. Metal-Nitrogen-doped carbon single-atom electroncatalysts for CO₂ electroreduction. *Compos. Part. B Eng.* **2021**, *220*, 108986. [CrossRef]

27. Liu, J. Catalysis by Supported Single Metal Atoms. *ACS Catal.* **2016**, *7*, 34–59. [CrossRef]

28. Lang, Q.; Yang, Y.; Zhu, Y.; Hu, W.; Jiang, W.; Zhong, S.; Gong, P.; Teng, B.; Zhao, L.; Bai, S. High-index facet engineering of PtCu cocatalysts for superior photocatalytic CO₂ reduction to CH₄. *J. Mater. Chem. A* **2017**, *5*, 6686–6694. [CrossRef]

29. Li, A.; Wang, T.; Chang, X.; Zhao, Z.-J.; Li, C.; Huang, Z.; Yang, P.; Zhou, G.; Gong, J. Tunable syngas production from photocatalytic CO₂ reduction with mitigated charge recombination driven by spatially separated cocatalysts. *Chem. Sci.* **2018**, *9*, 5334–5340. [CrossRef]

30. Zhang, X.; Han, F.; Shi, B.; Farsinezhad, S.; Dechaine, G.P.; Shankar, K. Photocatalytic Conversion of Diluted CO₂ into Light Hydrocarbons Using Periodically Modulated Multiwalled Nanotube Arrays. *Angew. Chem. Int. Ed.* **2012**, *51*, 12732–12735. [CrossRef]

31. Lee, S.; Jeong, S.; Kim, W.D.; Lee, S.; Lee, K.; Bae, W.K.; Moon, J.H.; Lee, S.; Lee, D.C. Low-coordinated surface atoms of CuPt alloy cocatalysts on TiO₂ for enhanced photocatalytic conversion of CO₂. *Nanoscale* **2016**, *8*, 10043–10048. [CrossRef]

32. Neatu, Ş.; Maciág-Aguillo, J.A.; Concepción, P.; García, H. Gold–Copper Nanoalloys Supported on TiO₂ as Photocatalysts for CO₂ Reduction by Water. *J. Am. Chem. Soc.* **2014**, *136*, 15699–15706. [CrossRef]

33. Kang, Q.; Wang, T.; Li, P.; Liu, L.; Chang, K.; Li, M.; Ye, J. Photocatalytic reduction of carbon dioxide by hydrosyndizin over Au-Cu alloy nanoparticles supported on SrTiO₃/SrTiO₂ coaxial nanotube arrays. *Angew. Chem. Int. Ed.* **2015**, *54*, 841–845. [CrossRef]

34. Baldovi, H.G.; Neatu, Ş.; Khan, A.; Asiri, A.M.; Kosa, S.A.; Garcia, H. Understanding the Origin of the Photocatalytic CO₂ Reduction by Au- and Cu-Loaded TiO₂: A Microsecond Transient Absorption Spectroscopy Study. *J. Phys. Chem. C* **2015**, *119*, 6819–6827. [CrossRef]

35. Zheng, M.; Jia, C.; Sharan, E.; Jiang, J.; Fan, W.; Zhao, X. Maximizing the Synergetic Effect of PdAu Catalysts on TiO₂(101) for Robust CO₂ Reduction:A DFT Study. *Appl. Surf. Sci.* **2021**, *563*, 150365. [CrossRef]

36. Ren, X.; Gao, Y.; Zheng, L.; Wang, Z.; Wang, P.; Zheng, Z.; Liu, Y.; Cheng, H.; Dai, Y.; Huang, B. Oxygen vacancy enhancing CO₂ electrochemical reduction to CO on Ce-doped ZnO catalysts. *Surf. Interfaces* **2021**, *23*, 100923. [CrossRef]

37. Yui, T.; Kan, A.; Saitoh, C.; Kioke, K.; Ibusuki, T.; Ishitani, O. Photochemical Reduction of CO₂ Using TiO₂: Effects of Organic Adsorbates on TiO₂ and Pd on TiO₂. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2594–2600. [CrossRef]

38. Kreft, S.; Wei, D.; Junge, H.; Keller, M. Recent advances on TiO₂-based photocatalytic CO₂ reduction. *Energy Chem.* **2020**, *2*, 100044. [CrossRef]

39. Zhou, W.; Guo, J.-K.; Shen, S.; Pan, J.; Tang, J.; Chen, L.; Au, C.-T.; Yin, S.-F. Progress in Photocatalytic O₂ Evolution by Au-Loaded TiO₂ Catalysts. *Acta Phys. Chim. Sin.* **2020**, *36*, 1906048. [CrossRef]

40. Blochl, P.E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979. [CrossRef]

41. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775. [CrossRef]

42. Kresse, G.; Hafner, J. Ab initio molecular-dynamics for open-shell transition-metals. *Phys. Rev. B* **1993**, *48*, 13115–13118. [CrossRef]

43. Kresse, G. Ab initio molecular dynamics for liquid metals. *J. Non-Cryst. Solids* **1995**, *192–193*, 222–229. [CrossRef]
44. 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. [CrossRef]

45. 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. [CrossRef]

46. Camellone, M.F.; Fabris, S. Reaction Mechanisms for the CO Oxidation on Au/CeO$_2$ Catalysts: Activity of Substitutional Au$^{3+}$/Au$^+$ Cations and Deactivation of Supported Au$^+$ Adatoms. *J. Am. Chem. Soc.* **2009**, *131*, 10473–10483. [CrossRef]

47. He, Z.; Wen, L.; Wang, D.; Xue, Y.; Lu, Q.; Wu, C.; Chen, J.; Song, S. Photocatalytic Reduction of CO$_2$ in Aqueous Solution on Surface-Fluorinated Anatase TiO$_2$ Nanosheets with Exposed [001] Facets. *Energy Fuel* **2014**, *28*, 3982–3993. [CrossRef]

48. Jónsson, H.; Mills, G.; Jacobsen, K.W. Nudged elastic band method for nding minimum energy paths of transitions. In *Classical and Quantum Dynamics in Condensed Phase Simulations*; Berne, B.J., Ciccotti, G., Coker, D.F., Eds.; World Scientific: Singapore, 1998; p. 385.

49. 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. [CrossRef]

50. Henkelman, G.; Jónsson, H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.* **2000**, *113*, 9978–9985. [CrossRef]

51. Henkelman, G.; Arnaldsson, A.; Jónsson, H. A fast and robust algorithm for Bader decomposition of charge density. *Comput. Mater. Sci.* **2006**, *36*, 354–360. [CrossRef]