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Effect of Defects and Photoexcited Electrons on CO2 Reduction using Supported Single Atom Catalysts

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Effect of Defects and Photoexcited Electrons on CO$_2$ Reduction using Supported Single Atom Catalysts

by

Junbo Chen

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of the

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Abstract

Excessive CO$_2$ emissions can negatively impact society and our planet. Reduction of CO$_2$ is one potential avenue for its abatement. One of the most significant challenges to reducing CO$_2$ is its extremely stable linear form. Experimentally, Cu/TiO$_2$ has shown promise for CO$_2$ photocatalytic reduction. Dispersed atomic catalysts can achieve high catalytic efficiency on a per atom basis. Active sites also typically having lower coordination number, and therefore may be more reactive. Using density functional theory and experimental techniques, we have investigated the role of surface oxygen vacancies (O$_v$) and photoexcited electrons on supported single atom catalysts and CO$_2$ reduction. Cu atoms with O$_v$ have shown to aid in the process of bent, anionic CO$_2$ formation. In the first step involving CO$_2$ dissociation (CO$_2^*$ → CO$^*$ + O$^*$), a single Cu atom in O$_v$ lowered the activation barrier to 0.10 - 0.19 eV, which could enable fast reduction of CO$_2$ even at room temperature, in agreement with experimental findings. A photoexcited electron model was shown to readily promote Cu binding to the surface vacancy, and CO$_2$ adsorption and direct dissociation. Finally we briefly compare our results to calculations of supported single Pt atoms to determine how metals besides Cu may behave as photocatalysts for CO$_2$ reduction. We found, similar to Cu, that a single Pt with O$_v$ can promote CO$_2$ dissociation. Our results show that tailoring TiO$_2$ surfaces with defects in conjunction with atomic catalysts may lead to useful catalysts in the photoreduction of CO$_2$. 
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Chapter 1

Introduction

Fossil fuel burning has been the primary means of energy production since the dawn of the industrial age. By burning these fuels to generate electricity and powered transportation, we also create an enormous amount of CO$_2$ in the atmosphere. Excessive CO$_2$ has shown a direct correlation to global warming due to the greenhouse effect. Increasing temperatures have caused serious and potentially irreversible impacts to our ecosystem, such as glacier melting in the arctic regions, rising sea levels, and extinction of coral and various sea life [6, 7]. Renewable energy, such as wind, solar and geothermal, have gathered global interest in eventually replacing current conventional energy sources.

Solar power is promising, and researchers are developing various methods to utilize solar power more effectively. CO$_2$ photoreduction is a potentially important reaction for removing this greenhouse gas from the atmosphere, and converting it to potentially useful products such as methane or methanol [8, 9]. Ever since Inoue et al. discovered photoelectrocatalytic reduction of CO$_2$ using photosensitive semiconductors, researchers have investigated converting CO$_2$ into hydrocarbons through photocatalysis [10, 11]. Supported Cu is a promising photocatalyst, especially dis-
persed atoms and clusters of Cu on TiO$_2$ [12]. Iyemperumal and Deskins found Cu sites likely contribute to improved photocatalysis by stabilizing surface adsorption of CO$_2$ on TiO$_2$. While they showed that small Cu clusters can indeed activate CO$_2$ to its bent configuration, forming an anion, they did not consider the presence of photoexcited electrons or the effect of surface defects, such as oxygen vacancies. Photoexcited electrons can further activate CO$_2$ to form an anionic species. He et al. showed that surface oxygen vacancies promote CO$_2$ binding, creating a CO$_2^-$ anion, which is widely believed as the first step for further photoconversion to other products [5]. Other work suggests that oxygen vacancies may have an important role in CO$_2$ reduction over Cu/TiO$_2$ photocatalysts[13, 14].

In this thesis we introduce some details on photocatalysts and the advantage of single atomic catalysts in Chapter 2. We then give a brief overview of the theory on density functional theory (DFT) and the modeling details in Chapter 3. In Chapter 4, we show our theoretical results on modeling Cu/TiO$_2$ catalysts with surface defects. We first modeled adsorbed Cu atoms on perfect TiO$_2$ surfaces and surfaces with oxygen vacancies. We also modeled CO$_2$ activation and reactivity over these Cu/TiO$_2$ surfaces. We further determined the effect of photoexcited electrons on Cu adsorption and CO$_2$ reduction. Our experimental results also compare Cu/TiO$_2$ catalysts with different type surfaces (stoichiometric and defective) to show the important role of Cu and $O_v$ in activating CO$_2$. Our experimental collaborators, Professor Gonghu Li’s group at the University of New Hampshire and Professor Ron Grimm’s group at Worcester Polytechnic Institute provided experimental support in the work. Finally, we briefly compare our results to calculations of supported single Pt atoms to determine how metals besides Cu may behave as photocatalysts for CO$_2$ reduction. These results suggest how single metal atoms, surface defects, and photoexcited electrons may work together to enable facile CO$_2$ photoreduction.
Chapter 2

Background Information

2.1 The Challenges of CO₂

Society’s reliance on fossil fuels has produced an enormous amount of CO₂ in our atmosphere, which directly impacts our ecosystem. CO₂ contributes directly to global warming as it traps heat from the sun. To reduce the atmospheric content of CO₂ is not an easy task as there are several challenges to surmount. One is that we are producing more CO₂ than the earth’s plants can convert naturally through photosynthesis, meaning that CO₂ levels are rising. The second is that CO₂ has various properties that make it difficult to capture, convert and store. In this section, we will discuss these two challenges of CO₂, and strategies for dealing with CO₂.

2.1.1 Excessive CO₂ and global warming

Excessive CO₂ in our atmosphere is the leading cause of global warming. In the past several decades, CO₂ concentrations have been increasing at a large rate. In Figure 2.1 is shown that the atmospheric carbon dioxide concentration has increased
from an average of 310 parts per million (ppm) in 1960 to 410 ppm in 2017.

Figure 2.1: Monthly mean atmospheric CO$_2$ concentrations at the Mauna Loa Observatory, Hawaii. The red curve represents the measured parts per million (ppm) of CO$_2$ in dry air. The black curve represents the seasonally corrected data. The image is in public domain from U.S. Department of Commerce at [1]

Greenhouse gases are the driving force of global warming and the inevitable consequences of global warming will and are affecting our ecosystem. Excessive CO$_2$ contributes to both climate temperature rising and increased ocean acidity, which can be harmful to the ecosystem. Excessive CO$_2$ reacts with water in combination with global warming and causes a lower pH value in the ocean. The increased ocean acidification could break the balance in ocean’s ecosystem therefore could negatively affect the food chain. A study showed that 25% of the human-created CO$_2$ has
entered the ocean, which reacts with water to produce carbonic acid \([6]\), leading to a more acidic ocean. The correlation between water’s \(\text{CO}_3^{2-}\) levels and atmospheric \(\text{CO}_2\) concentrations indicates that the more \(\text{CO}_2\) we produce, the more carbonate ions are consumed, therefore making the ocean more acidic. Ocean acidification is the direct cause of acid rain as the majority of rain consists of the evaporation of water from the ocean, in which could erode equipments in our infrastructure and harm plants’ growth.

2.1.2 \(\text{CO}_2\) properties

Carbon dioxide has a very inert molecular structure. \(\text{CO}_2\) is linear and has two stable \(\text{C} = \text{O}\) bonds, with a standard state free energy of formation \((\Delta G_f^0)\) of -394.4 kJ/mol \([15]\). In order to fully reduce \(\text{CO}_2\) to other products, one has to break a \(\text{C} = \text{O}\) bond. The double bond’s dissociation energy requires at least 749 kJ/mol, compared for instance to breaking a hydrogen bond in \(\text{H}_2\text{O}\) at 498.7 kJ/mol \([16]\). Because the amount of energy required to dissociate \(\text{CO}_2\) is so high, \(\text{CO}_2\) can be very unreactive.

![Figure 2.2: A sketch of linear to bent \(\text{CO}_2\) in a \(\text{CO}_2\) activation process. The structural change requires one electron transfer to the linear \(\text{CO}_2\) molecule. Carbon atoms are depicted in blue, and oxygen in green.](image-url)

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Activation of CO$_2$ may require bending the molecule from its linear structure. As shown in Figure 2.2, linear CO$_2$ has a bond angle (O-C-O) of 180°, and after one electron transfers to the linear molecule it may form a bent structure. The extra electron alters the electron configuration of the CO$_2$ molecule, which changes the linear form to a bent form, with approximately a bond angle 135°. CO$_2$ activation is believed to the first step in CO$_2$ reduction[5, 17]. In the anionic bent form, CO$_2$ can be directly dissociated into CO and O or hydrogenated to form either HOCO (RWGS, Reverse Water-Gas Shift reaction) or HCOO (Formate pathway)[17]. These three pathways all originated from this bent activated CO$_2$ structure. In Chapter 4, we will focus on the first step of direct dissociation pathway.

### 2.1.3 Strategies for Dealing with CO$_2$

Currently, there are two main ways to deal with excessive CO$_2$ in the atmosphere. One is carbon capture and storage (CCS). CCS utilizes adsorption and membrane technologies to separate and capture CO$_2$ from flue gases[18, 19] or the atmosphere itself. The captured CO$_2$ is then transported and deposited at a storage site, where it will kept from being released to the atmosphere. The mature technology of CCS has been applied industrially to natural gas processing and ammonia production, which both emit a large amount of CO$_2$[20]. Directed air capture, which now broadly defined as CO$_2$ extraction from the atmosphere, shows some possibility for direct CO$_2$ capture, but the technology is still in its infancy given carbon dioxide’s low concentration (400 ppm, or 0.04%) in the atmosphere[21].
Figure 2.3: A scheme showing solar conversion over a photocatalyst particle. The photoexcited electrons can be utilized to reduce CO$_2$; while the photoexcited holes can be used to oxidize water to generate hydrogen and oxygen.

Another promising strategy to remove CO$_2$ is through chemical conversion, or CO$_2$ reduction. Solar energy utilization in CO$_2$ reduction can be summarized in a two step process; first capturing the CO$_2$ and converting it into another chemical form, such as methane, methanol, etc., then either storing or using the converted chemicals\cite{22}. Photocatalysis, similar to nature’s photosynthesis $^1$, can use a semiconductor to absorb certain light and excite electrons. The photoexcited electrons and corresponding positively charged holes may enable reduction and oxidation reactions on the surface of the semiconductor or accompanying co-catalyst. In Figure 2.3, we show a solar conversion process using a photocatalyst in a particle form, which includes both reduction and oxidation reactions. We will discuss the mechanism of

\footnotesize{$^1$A photosynthesis process utilizes an enzyme (chlorophyll) to convert solar energy to reduce CO$_2$ to carbohydrates in a plant, while oxidizing H$_2$O to O$_2$.}
photocatalysis in detail in section 2.2.1. But in this Figure 2.3, the advantage of a photocatalyst is two-fold: the reduction reactions can convert CO\(_2\) to reuse the carbon we have produced, and the oxidation reactions can split water into hydrogen as an alternative clean fuel. This thesis focuses on the conversion of CO\(_2\) (reduction reaction) via photocatalysis.

2.2 CO\(_2\) Photoreduction on Semiconductors

CO\(_2\) photoreduction allows the conversion of carbon dioxide into potential valuable fuel sources, such as methane and methanol. Photocatalysts are designed and engineered to take advantage of solar energy to absorb and convert molecules through catalytic reactions. This section will introduce how semiconductor photocatalysts work to effectively to reduce CO\(_2\), and compares different types of photocatalysts.

2.2.1 Fundamentals of Photocatalysis

Photocatalysts absorb solar energy to accelerate a reaction. An example of a photoreaction in nature is photosynthesis in plants. Plants use solar energy to convert CO\(_2\) and water into glucose and oxygen. Glucose stores solar energy in a chemical form. Photocatalysis mimics the Calvin Cycle in green plants to fixate and convert CO\(_2\) to other chemicals, like solar fuels. Key to viable CO\(_2\) conversion are cheap, effective photocatalyst materials.
In photocatalysis, semiconductors absorb light, limited by the semiconductor’s band gap. As shown in Fig 2.4, a band gap ($E_g$) is defined as the energy difference between filled and unfilled electronic states, or the valence band (VB, filled area) and the conduction band (CB, unfilled area). When an electron ($e^-$) leaves the valence band to enter the conduction band due to light excitation, a hole is created in the valence band. A hole ($h^+$) is the lack of an electron at a position where it can or should be. The net effect of a hole is that the atom is positively charged because of the missing electron. In the oxidation process, photoexcited holes can be used to oxidize $\text{H}_2\text{O}$ to $\text{O}_2$ and $\text{H}_2$, which happens after photoexcitation. This oxidation reaction is an important aspect to study in order to have a complete picture of the semiconductor’s photocatalysis. The scope of this thesis however is on the $\text{CO}_2$ reduction reaction.

Figure 2.4: A simple diagram of a semiconductor band structure showing the band gap between the upper edge of the valence band and the lower edge of the conduction band. The image is available by Creative Commons from Wikimedia Common [2].
On the reduction side of the semiconductor, photoexcited electrons in the conduction band can react with surface species in a reduction reaction. During CO$_2$ reduction, CO$_2$ can receive a photoexcited electron and become reduced to CO$_2^-$, making it an unstable species which can react further. When an electron and hole recombine before reacting on the surface, heat is generated and the photoexcitation efficiency for CO$_2$ reduction diminishes since the concentration of electrons and holes decreases.

### 2.2.2 A Comparison of Semiconductor Photocatalysts

Various promising semiconductors, such as oxides, sulfides, and phosphides have been studied. A semiconductor photocatalyst with a small band gap has the ability to absorb a larger part of the visible light spectrum [23]. Each type of semiconductor has advantages and disadvantages such as being n-type (electron rich, or having electrons as the majority carrier) or p-type (holes rich, or having holes as the majority carrier), as well as having other different physical properties. For example, sulfide semiconductors, such as CdS, were the core component in one of the first efficient photovoltaic (PV) cells reported[24]. However, the disadvantage of sulfide semiconductor photocatalysts is their instability in aqueous environments. In water the oxidation of the lattice S$^{2-}$ ions and eventual conversion to sulfates can occur, therefore altering the catalyst’s structure and properties[25].

The most widely studied photocatalyst semiconductor, and the focus of this work, is TiO$_2$. TiO$_2$ (titania) has shown strong promise as an effective CO$_2$-reducing photocatalyst. TiO$_2$ is abundant in the earth, cheap to produce, resistant to photocorrosion, and non-toxic [26]. Because of these aspects, TiO$_2$ has attracted interest as a photocatalyst, and especially many features have been studied, such as its crystal lattice, surface properties, charge transfer, etc. [11]. TiO$_2$ is often more
efficient when paired with a co-catalyst, usually noble-metal nanoparticles[23]. In an experimental paper, it was first reported that Rh/TiO$_2$ can promote the formation of bent CO$_2^-$ anion radicals[27], which are important towards CO$_2$ reduction. However, rhodium or other noble metal cannot be a long-term solution because of the high cost of these co-catalysts, which increases the cost of making these photocatalyst for large scale CO$_2$ conversion. For instance, the price for rhodium is $1,500 per ounce, and platinum $1,000 per ounce as of January 2018 [28]. As an economical alternative, copper ($0.2 per ounce) has shown promise as a co-catalyst with TiO$_2$[13, 14, 29]. In this work, we will focus on Cu/TiO$_2$ catalysts with surface defects to determine the role of these defects in activating and converting CO$_2$.

2.3 Surface Features and TiO$_2$ Photocatalysis

Figure 2.5: The top (upper figure) and side (lower figure) views of the anatase (101) surface. Each of the surface oxygen atoms (O$_{2c}$) bonds with two Ti atoms. Each of the sub-surface oxygen atoms O$_{3c}$ bonds with three Ti atoms. The red spheres represents oxygen, and cyan spheres represent titanium.
In photocatalysis, most of the reactions occur at the surfaces of the catalyst. Therefore understanding the surface features of TiO$_2$ becomes essential in effective photocatalyst design, such as how co-catalysts interact with the TiO$_2$ surfaces and how various types of surface defects affect the catalysis. The surface of these semiconductors can catalyze reactions with a co-catalyst, typically a transition metal such as Au, Pt, or Cu, which can have several possible structures, such dispersed atoms, nanoclusters, or nanoparticles. On a TiO$_2$ surface, surface defects such as interstitial impurities or oxygen vacancies can create adsorption and active sites, possibly accelerating photoreactions.

In this work, we focus on the anatase (101) surface, which is the most stable surface of anatase and shown in Figure 2.5. Each of the surface oxygen atoms (O$_{2c}$) bonds with two Ti atoms. Many studies focus on the more stable surface facets of TiO$_2$ such as the (101) surface of anatase or the (110) surface of rutile [30] to understand the stability of their surface structures[31], binding to different co-catalysts[32, 33, 12], and the selectivity of bent to linear CO$_2$[5, 34]. This high selectivity to bent CO$_2$ over linear CO$_2$ suggests more charge has been transferred to CO$_2$ in order to activate it. CO$_2$ activation occurs as the stable linear structure transforms to a bent structure.
2.3.1 Surface Defects

Figure 2.6: A defective TiO$_2$ anatase (101) surface. A surface oxygen vacancy is indicated by the arrow and "O$_v$". The two adjacent Ti atoms are reduced to Ti$^{3+}$. Other Ti atoms are formally Ti$^{4+}$. The blue atoms represent Ti, red atoms represent O.

Defects can be formed in TiO$_2$, for example, during thermal treatment and ion bombardment during preparation[35], but they also naturally occur. There are a variety of point defects on both surfaces and in the bulk, such as surface oxygen vacancies or interstitial atoms. In this thesis we focus on the surface oxygen vacancy of titania. Each oxygen vacancy creates two reduced titanium, Ti$^{3+}$. Ti atoms are formally Ti$^{4+}$ in stoichiometric TiO$_2$, and as the O$^{2-}$ are removed two electrons remain that reduce two Ti$^{4+}$, or O$^{2-}$ → O$_v$ + $\frac{1}{2}$O$_2$ + 2e$^-$. In Figure 2.6, the
removal of the oxygen vacancy creates two nearby Ti$^{3+}$.

Surface defects have been shown to be potentially important in promoting CO$_2$ activation from both theoretical and experimental studies. In a theoretical study by He et al.[5], the reduced TiO$_2$ surface was examined closely using molecular modeling methods to determine the effect of oxygen vacancies on CO$_2$ reduction. The study concluded that the reduced (defective) anatase (101) surface is much more favorable than the stoichiometric surface for CO$_2$ binding and charge transfer. CO$_2$ favors binding to oxygen vacancies (O$_v$) due to the localized electrons near the O$_v$, especially the under-coordinated Ti atoms, and reduced surfaces have a higher probability for CO$_2$ adsorption and activation. In other experimental studies, Liu et al.[13, 14] applied X-ray photoelectron spectroscopy (XPS) and in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) to confirm that CO$_2$ can spontaneously dissociate into CO + O under dark conditions (CO$_2^*$ → CO$^*$ + O$^*$). They proposed a mechanism where CO$_2$ binds in the region of the O$_v$ and dissociates to fill it.

### 2.4 Single Atomic Catalysts

Single atomic catalysts (SACs) have a single atom (or a few atoms) embedded in a matrix or on a support [36, 37]. Figure 2.7 shows a titania supported SAC with Cu atoms adsorbed on the surface. The primary reason for using SACs stems from lowering the catalyst cost while enhancing the efficiency of the catalysts. By depositing a metal catalyst at the atomic scale and dispersing them, SACs also expand the amount of active sites by isolating these single atoms. When atoms aggregate together, the surface area to volume ratio of the metal catalyst drastically reduces therefore making the catalyst less effective. DeRita et al. discovered that an
isolated single Pt atom had a two-fold turnover frequency (TOF) increase and lower activation energy than a 1 nm Pt nanocluster [38] for the CO oxidation reaction. Qiao et al. have also found that single Pt atom catalysts had increased efficiency for CO oxidation on a FeO$_x$ support [39]. Of particular importance is the CO$_2$ reduction reaction, which can curtail this greenhouse gas. Several reports describe the use of supported single atom catalysts for CO$_2$ reduction[40, 41]. These key studies suggest the potential of SACs for photocatalysis. We will discuss further Cu/TiO$_2$ photocatalysts that have been studied by experimental and computational means.

Figure 2.7: A top view of a titania surface with single atomically dispersed Cu. The Ti atoms are spheres in cyan, O in red, and Cu in orange.
2.4.1 Experimental Results of Single Atomic Catalysts

For CO$_2$ reduction, Cu/TiO$_2$ has shown some promising results in converting CO$_2$ into CO [13, 14, 29]. Experimental work indicates Cu clusters on TiO$_2$ with surface oxygen vacancies can enable CO$_2$ dissociation, even without light[13, 14]. For other reactions, Matsubu et al. [40] showed that isolated Rh on TiO$_2$ was highly selective to CO in the reverse water gas shift reaction, where nanoparticles of Rh selectively produced CH$_4$ on the same support. Kwak et al. [41] demonstrated that atomically dispersed Pd on a Al$_2$O$_3$ support showed favorable reactivity compared to Pd clusters for the CO$_2$ reduction reaction due to the low coordinated atomic Pd atoms. Other work highlights how single-atom catalysts can be active for CO$_2$ reduction, such as supported atomic Cu[14, 29, 42], Mn[42], Pd[42] on TiO$_2$ as support and Co on metal-organic framework support[43].

2.4.2 Computational Studies of Single Atomic Catalysts

There have been several modeling studies of SACs that highlight adsorption and reaction mechanisms for the CO$_2$ reduction reaction and on how the single metal atoms interact with the support material. In a theoretical investigation on Cu/TiO$_2$ photocatalysts on CO$_2$ reduction, Iyemperumal and Deskins studied small clusters of Cu (1-4 atoms) and found that Cu in a dimer form enabled strong bent CO$_2$ formation over linear CO$_2$, which is important in activating CO$_2$[12]. Bent CO$_2^-$ were shown to be more stable than linear CO$_2$, and also charge transfer activated the bent molecule to an anion form, CO$_2^-$. To further support the viability of Cu for CO$_2$ reduction, Liu et al. suggested that small Cu clusters (Cu$_4$) may be excellent and efficient catalysts for the development of low-pressure CH$_3$OH synthesis from catalytic conversion of CO$_2$[44]. On graphite carbon nitride (g-C$_3$N$_4$) support, Gao
et al. demonstrated single atomic Pd/Pt were a viable catalyst to convert CO$_2$ to HCOOH on g-C$_3$N$_4$ [45]. Besides CO$_2$ reduction, several computational studies also provided fundamental insight on how single metal atoms interact with a support, such as Pt[32, 46], Au[47, 48], Ag[47, 48], Cu[29, 12, 49, 47] on TiO$_2$. However, these key computational papers have not yet fully explained the effect of surface oxygen defects for Cu/TiO$_2$ catalysts, which is the focus of the current research.
Chapter 3

Methodology

Quantum mechanics has allowed the use of mathematics to describe how atoms and molecules interact to each other. The advance of both mathematic techniques (e.g. density functional theory) and computational tools (high performance computer and parallel computing) have made the use of these complex mathematic models solvable in a realistic time-frame. With such theoretical results, we can validate experimental data and provide details on chemical systems, for instance possible reaction mechanisms.

This chapter will cover many of the concepts used in ab-initio quantum modeling, including the fundamental equations used in density functional theory (DFT), electron density, wavefunctions, exchange-correlation functionals, and self-consistent calculations. We will also discuss the DFT+D and +U method and how they modify the theory and improve DFT results. In the latter part of this section, we will introduce the plane-wave basis sets and periodic boundary condition (PBC), which are essential for modeling surfaces, and the nudged elastic band (NEB) method for seeking the minimum energy pathway (MEP) and calculating reaction barriers.
3.1 Schrödinger Equation and Density Functional Theory

Density functional theory (DFT) is a quantum mechanical modeling method used to model the electrons of atoms and molecules. DFT has been widely used in research and have useful applications in calculating heats of adsorption, vibrational frequencies, heats of activation, etc.[4] The basis of DFT is the time-independent Schrödinger equation (Equation 3.1).

\[
\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i}^{N} U(r_i,r_j) \right] \Psi = E \Psi \tag{3.1}
\]

Here \( m \) is the electron mass, \( \hbar \) is Planck’s constant and \( E \) is the total energy of the system. Inside the bracket, in order, are the kinetic energy of all the electrons, the interaction energy between all electrons and the atomic nuclei, and the interaction energy between different electrons. The wavefunction \( \Psi \) is a function of the spatial coordinates (\( x,y,z \) in Cartesian coordinates) of all the electrons in the system. By knowing the wavefunction of a particle, we can understand and predict the behavior of that particle at any point in space. For a many-electron problem (such as hundreds of molecules), the Schrödinger equation (Equation 3.1) takes into account the electron-electron interactions. Notice that as more electrons are introduced, the many-electron problem becomes very difficult to solve for its total energy.

The Schrödinger equation is also an eigenproblem given its mathematical form, such that \( \hat{H} \Psi = E \Psi \), where \( \hat{H} \) is the Hamiltonian operator\(^1\) and \( E \) is the corresponding eigenvalue, and is the total energy of the system. Many powerful methods for solving the Schrödinger equation were developed in the past, but the calculations

\(^1\)The Hamiltonian relates the total energy of the system, and contains the kinetic and potential energy terms in the brackets of Equation 3.1.
became practically impossible for large and complex systems.

\[ n(r) = \sum_i \theta_i^*(r) \theta_i(r) \]  

(3.2)

To get a reasonable estimate of both the electrons’ positions and their energies, the electron density \( n(r) \) simplifies this many-electron problem to a probability problem for DFT. In Equation 3.2, the sum over one-electron wavefunction \( (\theta_i(r)) \) products is the probability of the electrons occupying some specific coordinates, or \( r \). Each of the wavefunctions in Equation 3.2 \( \theta_i \) stands for a one-electron wavefunction, and the total wavefunction \( \Psi \) can be found by multiplying wavefunctions of all the electrons together \( (\theta_1 * \theta_2 * \theta_3 * ...) \). For fully spin-unrestricted wavefunctions (independent wavefunctions for spin up and spin down electrons) we would calculate each one-electron wavefunction independently for each spin state.

With the definition of electron density (a quantum mechanical concept) that transforms the many-electron problem to a probability problem, the conceptual roots of DFT were supported theoretically after Hohenberg and Kohn [50] derived two theorems in the mid-1960s, known as the Hohenberg-Kohn Theorems (H-K Theorem):

**Theorem 3.1.1** The ground-state energy from Schrödinger’s equation is a unique functional of the electron density.

**Theorem 3.1.2** The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.

The first H-K Theorem states that there is only one functional of the electron density that can represent the total energy of a system of electrons. A functional
takes a function and determines a single number from that function.\(^2\) Finding that unique density therefore will yield the total energy of the electrons. The second H-K Theorem gives us a strategy to solve the Schrödinger equation, in which if we have a "true" functional to find the energy, then we could modify the electron density until the energy, or the eigenvalue of the Schrödinger equation (an eigenfunction form), is minimized. In practice, we can apply the variational principle \(^3\), to determine an estimate of the minimum energy.

Later on Kohn and Sham \([51]\) derived the Kohn-Sham (KS) equations which have the form:

\[
\left[\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r)\right]\theta_i(r) = \epsilon_i \theta_i(r) \tag{3.3}
\]

\[
V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3r' \tag{3.4}
\]

\[
V_{XC}(r) = \frac{\delta E_{XC}}{\delta n(r)} \tag{3.5}
\]

Compared to the Schrödinger equation (Equation 3.1), the KS equations consist of single-electron wavefunctions \(\theta_i\) (not \(\Psi\)), which are the same wavefunctions as in the electron density Equation 3.2. In addition to the kinetic energy term, Equation 3.4 describes the Coulomb repulsion between electrons, which is an average potential created by the electrons. A key assumption, which simplifies solving these equations, is that the kinetic energy is calculated for non-interacting electrons. Making this assumption simplifies solving the equations, but adds a needed correction

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\(^2\)As an example, for the function \(f(x) = x^2 + 1\), the functional \(F\) is an operator such that \(F([f] = \int_{-1}^{1} f(x) dx\), and we should get \(F[f] = \frac{8}{3}\).

\(^3\)In general, variational principle is defined as finding functions that extremize the values depending on the purpose of the calculation; in the current case we seek to find the minimum energy.
term $V_{XC}$, which is the derivative of exchange correlation energy with respect to electron density Equation 3.5, and is known as the exchange-correlation functional.

An exact exchange and correlation functional is not easy to find knowing it exactly would be equivalent of exactly solving the Schrödinger equation. Approximate forms of $V_{XC}$ are used since its true form is not known. The earliest approximation is the local density approximation (LDA), which uses a uniform electron gas as a reference and provides an energy that depends only on the electron density at specific points (local density) in space. This method is a rather crude approximation of this XC functional. Therefore, to get a reasonable estimate of the total energy, the choice of the XC functional is important. We can refer to Jacob’s ladder, coined by Perdew and co-workers[52] who borrowed a Biblical reference to the discovery of XC functionals: the higher on the ladder the more accurate the exchange correlation functional is (or closer to Heaven than Earth). The caveat is that more accuracy typically comes with more computational cost for the XC functionals. Perdew Burke and Ernzerhof (PBE)[53] published a XC functional (GGA functional) that has been accepted by the DFT community to have relatively good accuracy and lower computational cost compared to functionals higher on the ladder, such as meta- and hyper-GGA functionals.

Lastly, with all the ingredients to perform the calculations in place, we can iteratively solve the KS equations in a process shown in Figure 3.1. The reason for the iteration is to find the energy minimum of the Schrödinger equation. see Theorem 3.1.2. The problem is a mean-field problem where the Hartree potential, Equation 3.4, is based on the average potential or density of each electron. That is, the potential that one electron feels from the other electrons is an average potential.

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$V_{XC}^{GGA}(r) = V_{XC}[n(r), \Delta n(r)],$ which is a higher XC functional than LDA that only uses the electron density $V_{XC}^{LDA}(r) = V_{XC}[n(r)]$. 

---

4The generalized gradient approximation (GGA) expresses the exchange and correlation functional in terms of both the local electron density and gradient in the electron density such that $V_{XC}^{GGA}(r) = V_{XC}[n(r), \Delta n(r)],$ which is a higher XC functional than LDA that only uses the electron density $V_{XC}^{LDA}(r) = V_{XC}[n(r)]$.
created by other electrons. A real system would have the electron densities (and hence potentials) responding instantaneously to changes in other electrons. For the DFT procedure, the electron density is composed of all the electrons and depends on the potentials (including Hartree potential, XC functionals and ionic potentials) of all the electrons. Therefore, every time when one electron changes, all the others change, and we have to re-iterate until the electron densities are self-consistent. A self-consistent calculation flowchart is shown in Figure 3.1. With a trial electron density, we can solve the KS equations to find the single-particle wave functions. Then we calculate a new electron density based on these wave functions. If the new electron density agrees with the trial electron density, then we have our solution to the KS equations. If not, we go back to the second step with an updated electron density, which can be adjusted by a new geometry or set of coordinates of electrons (geometry optimization). Normally, the self-consistent calculation stops when the energy changes between each wavefunction/electron density are below some threshold.
3.1.1 DFT+D and +U method

A missing element of DFT are the dispersion interactions\textsuperscript{5}. The dispersion interactions among molecules can be crucial to include in treating molecules that are non-polar but still exhibit attraction due to dispersion forces. The DFT+D method was developed to take long-range dispersion forces into account, which are missing in DFT. In this thesis, we used Grimmes’ D3 method\textsuperscript{[54]} which has the form:

$$E_{DFT-D} = E_{DFT} - S \sum_{i \neq j} \frac{C_{ij}}{r_{ij}^6} f_{damp}(r_{ij})$$  \hspace{1cm} (3.6)

In Equation 3.6, $C_{ij}$ is the dispersion coefficient for atoms i and j, which are\textsuperscript{5} also known as van der Waals interactions or London forces.

\textsuperscript{5}also known as van der Waals interactions or London forces
tabulated, and $f_{damp}(r_{ij})$ is a damping function to avoid unphysical behavior of the dispersion terms for small distances. $S$ is a scaling factor that applies to all atoms. We used Becke-Johnson damping[55] with the D3 method.

Another problem with DFT is the so-called self-interaction contribution between an electron and itself. The Hartree potential in Equation 3.4 actually includes an unphysical repulsive interaction between the electron and itself because each electron belongs to the total electron density $^6$. Due to this term, when we have unpaired electrons present in a system (a surface with an oxygen vacancy, for example), the self-interaction contribution (in literature sometimes are called self-interaction error) becomes more relevant which might deviate the total energy away from the actual energy or lead to incorrect wavefunctions. Therefore, to deal with this "artifact" in KS equations, it is a common practice to apply either Hubbard U (+U) method [56] or hybrid functionals in systems with excess electrons. In this thesis, we used the +U method as this approach is computationally more feasible than the hybrid functionals. More details on +U methods can be found in ref[4].

3.2 Plane-wave Basis Sets and Modeling Periodic Systems

A basis set is a set of functions that are used to represent the wavefunction in DFT in order for computers to solve the KS equations. Using a basis set with more functions gives more accuracy at the cost of more calculations. A basis set can be composed of mathematical functions that mimic atomic orbitals, such as Slater Type Orbitals (STOs) or Gaussian Type Orbitals (GTOs). Many computational packages

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$^6$A way to think of this self-interaction is the electron and its interaction to itself have been accounted for in the Hartree potential, which is incorrect.
(NWChem\cite{57}, Gaussian\cite{58}, etc.) use Gaussian type basis sets to model molecular systems. For example, STO-3G \footnote{STO-3G is a minimum basis set that takes three primitive Gaussian Orbitals to fit one Slater Orbital. A minimum basis set is where only sufficient orbitals are used to contain all the electrons in the neutral atom. The core and valence orbitals are represented by the same number of primitive Gaussian functions. The wavefunctions of STO-3G look like $\theta_{STO-3G} = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$, in which each $\phi$ is a Gaussian Type Orbit that has the form $\phi = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{4}}e^{-\alpha r^2}$}. Bigger basis sets are typically more accurate but require more simulation time. For example, when calculating the ionization energy (with B3LYP XC functionals) of a CH$_4$ molecule, STO-3G is less accurate but requires less time than the cc-PVTZ basis set \cite{4}. However, when dealing with solids, the Gaussian basis sets become inefficient and nearly an impossible task for such a large system. For periodic crystals the plane-wave approach can make the calculations manageable with Bloch’s theorem which states that the solution of the Schrödinger equation with periodic boundary conditions has this form:

$$\theta_k(r) = e^{i k \cdot r} u_k(r) \quad (3.7)$$

$$u_k(r) = u_k(r + n_1 a_1 + n_2 a_2 + n_3 a_3) \quad (3.8)$$

In Equation 3.7, the wavefunction now is represented in $e^{i k \cdot r}$ and $u_k(r)$, with vectors $r$ in real space and vectors $k$ in reciprocal space (or k space). The functions $e^{i k \cdot r}$ are frequently referred to as plane waves, therefore calculation based on Bloch’s theorem with periodicity are called plane-wave calculations. $u_k(r)$ on the other hand is periodic in space with the same periodicity as the unit cell, which has a form in Equation 3.8 that expands like $u_k(r + n_1 a_1 + n_2 a_2 + n_3 a_3)$ for any integer $n_1$, $n_2$, $n_3$. Typically plane waves as a function of the reciprocal lattice vectors (G) are used for $u_k$. Now combining the plane-wave basis sets into the KS equations, we have:
\[ \theta_k(r) = \sum_{|G+k|<G_{\text{cut}}} c_{k+G} \exp[i(k + G)r] \] (3.9)

where \( G \) represents the set of lattice vectors in reciprocal space, and \( G_{\text{cut}} \) is related to a cut-off energy \( E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2 \) such that the summation only includes functions with kinetic energy less than the cut-off energy. In solid states (like crystals), a large cut-off energy is needed due to the nuclei. Conceptually, to deal with this large cut-off energy, a pseudopotential replaces the core electrons with a smoothed density/potential to capture the various important physical and mathematical properties of the true electron density[4]. The quantum chemistry package we used is CP2K[59], which uses a mixed plane-wave/Gaussian basis set and pseudopotential by Goedecker-Tetter-Hutter [60] and double \( \zeta \) valence potential (DZVP) for valence electrons treatment.

Figure 3.2: Bulk Cu consists of (a) a unit cell with 4 face centered cubic (FCC) Cu atoms, with red lines indicating the unit cell boundaries. (b) A unit cell within a larger Cu crystal with the red lines indicating the boundaries of the unit cell. The spheres represent Cu atoms.
To demonstrate what periodic boundary conditions (PBC) are, we show a face centered cubic (FCC) Cu unit cell in Figure 3.2a. In Figure 3.2b is shown a Cu unit cell which is part of a bulk Cu crystal. However, modeling bulk structures is different from modeling surfaces. To demonstrate how to model a surface, in Figure 3.3a is shown the slab model. A slab, or layer, of the material is modeled and a vacuum space is created between slabs. Because of the periodic boundary conditions the slab is repeated in all directions. The empty space is needed to separate periodic images and avoid artificial surface interactions between slabs. In Figure 3.3(b) a TiO$_2$ (Ti$_{96}$O$_{192}$) cell structure is shown as the repeating cell given in (a). Here we show three bi-layers of TiO$_2$ and fix the atoms at the bottom of the slab. The frozen bottom layer will mimic the bulk structure and will not have any adsorbate interactions. A middle layer works as a transition layer between the surface and bulk, and the top layer will behave as the surface and adsorb and react with molecules.
Figure 3.3: A surface slab for TiO$_2$ with (a) a slab supercell repeated in different directions due to periodic boundary conditions. Red lines indicate the super cell (or repeating unit) boundary. (b) Further details on the TiO$_2$ slab, with the bottom layer fixed to mimic bulk layer, and the indicated surface where reactions may be modeled. The spheres in red represent oxygen atoms, and in gray represent titanium atoms. The red dashed line is the super cell boundary.

3.3 Nudge Elastic Band Calculations

In this thesis we located transition states, or the reaction barriers (or activation energies) for reactions. This barrier is crucial to predicting a reaction rate constant $k = A \cdot \exp\left(\frac{\Delta E}{k_B T}\right)$, where $\Delta E$ is the activation energy, and $A$ is a pre-exponential factor in the Arrhenius equation. The nudged elastic band (NEB) method was developed by Jónsson and co-workers [61] as a refinement of an earlier ”chain-of-states” methods for locating the transition state of a reaction. The purpose of a chain-of-states calculations is to find the minimum energy path (MEP) between two
local minima. The chain-of-states calculations can be expressed mathematically for a set of images $r_0, r_1, \ldots, r_p$ (each image represent a geometry along an energy pathway) by defining a function:

$$M(r_0, r_1, \ldots, r_p) = \sum_{i=1}^{P-1} E(r_i) + \sum_{i=1}^{P} \frac{K}{2} (r_i - r_{i-1})^2$$ (3.10)

In Equation 3.10, $E(r_i)$ is the total energy of the $i$th image. The second term describes fictional spring forces that connect each image to neighboring images along the path. An example of a potential energy surface is shown in Figure 3.4. Indicated by numbers are possible images or geometries along the minimal energy path. If no spring forces are applied, then images 2 and 3 (and possibly 4) will optimize to image 1, while images 5 and 6 will optimize to image 7. Not having a way to constrain the images along the path would not reveal the minimal energy pathway. The spring forces ensure that each image is "pulled" along the path to maintain a geometry along that path. During the nudged elastic band optimization, each image will continue to move in the direction of arrows in Figure 3.4 until each image reaches the true minimum energy pathway.

NEB calculations are typically computationally demanding since each of the images (or replica) is a DFT calculation on its own. Henkelman and co-workers [62, 63] have implemented and updated a Climbing Image Nudged Elastic Band (CINEB) method for the transition state calculation, which is the method that we used in this thesis. CINEB has a small modification to the NEB method in which the highest energy image is driven up to the saddle point[64]. Instead of the harmonic spring force, the true force at this image along the tangent is inverted. Hence this image seeks to maximize its energy along the direction that is tangent to the energy path. Therefore when this image converges, it has to reach the saddle point since it
should be the maximum along the energy pathway. For more details on transition state theory, electronic structure, and materials modeling, useful information can be found in ref[4, 3, 65].

Figure 3.4: A potential energy surface between two states to demonstrate the Nudged Elastic Band method. The yellow dashed line represents the minimum energy pathway (MEP) between image/state 1 and 7, where the numbered dots represent a geometry on an energy path pathway (not the minimum pathway), and the arrows indicate the direction for converging each geometry towards this MEP. This figure is adapted from ref[4].
Chapter 4

Synergy between Defects, Photoexcited Electrons, and Supported Single Atom Catalysts for CO$_2$ Reduction

For the experimental part of this research, please refer to Appendix B.
4.1 Introduction

Small clusters and single-atom catalysts can have potentially increased reactivity compared to larger clusters or nanoparticles. Such catalysts have a single atom (or a few atoms) embedded in a matrix or on a support[37, 36, 66, 67, 68, 69, 70, 71]. For instance, recently DeRita et al. discovered that an isolated single Pt atom on TiO$_2$ had a two-fold turnover frequency increase and lower activation barrier than a 1 nm Pt nanocluster for the CO oxidation reaction[38]; other work also showed single atom Pt can catalyze CO oxidation in ceria [72] and FeO$_x$ [39] support. Of particular importance is the CO$_2$ reduction reaction, which can curtail this greenhouse gas. Several reports describe the use of supported single atom catalysts for CO$_2$ reduction[40, 41].

Reduction of CO$_2$ can produce products such as methane or methanol [10, 23, 73, 8, 15, 9]. Supported Cu is a promising catalyst[13, 74, 75, 76, 77], especially small Cu clusters or atoms on TiO$_2$[44, 78, 79, 42]. Other work highlights how sub-nanometer catalysts can be active for CO$_2$ reduction, such as supported sub-nanometer size, Pt[45, 80] Mn[42], Pd[42] and Ir[81] on TiO$_2$, graphene [82] and metal-organic framework[43]. Of note, experimental work indicates Cu clusters on TiO$_2$ with surface oxygen vacancies can enable CO$_2$ dissociation, even without light[13, 14].Surface features, such as oxygen vacancies, may play an important role in CO$_2$ reduction over metal oxide catalysts[83, 84, 5, 34, 85, 86, 87, 88, 89, 90, 91].

Density functional theory (DFT) has been used to model supported sub-nanometer metal catalysts[92, 93, 94, 46, 32, 95, 96, 49, 97, 98, 99, 100, 47]. For instance modeling CO$_2$ reduction over Pt or Ag clusters on TiO$_2$ has been shown to enable CO$_2$ activation[33, 101, 102]. In our previous work we modeled adsorbed Cu atoms on TiO$_2$ surfaces as photocatalysts [29, 12]. We found Cu sites likely contribute to the
improved photocatalysis by stabilizing surface adsorption of CO₂ on TiO₂. Other authors have also modeled surfaces with oxygen vacancies and concluded that surface defects can enhance the CO₂ adsorption properties [5, 34, 103, 104, 105, 88]. Still, how oxygen vacancies and photoexcited electrons may interact with supported metal atoms is not fully clear. Atomic-level details on the interactions between support, single atoms, excited electrons, and defects for catalytic reactions, such as CO₂ reduction, need further elucidation since understanding the role of these various features may guide better catalyst design.

In this work we have modeled using DFT adsorbed Cu atoms on perfect TiO₂ surfaces and surfaces with oxygen vacancies. We also modeled CO₂ activation and reactivity over these Cu/TiO₂ surfaces. We further determined the effect of photoexcited electrons on Cu adsorption and CO₂ reduction. Our experimental results also compare Cu/TiO₂ catalysts with different type of adsorption surface (stoichiometric and defective) to show the important role of Cu and O_v in activating CO₂. Finally, we briefly compare our results to calculations of supported single Pt atoms to determine how metals besides Cu may behave as photocatalysts for CO₂ reduction. These results show how single metal atoms, surface defects, and photoexcited electrons may work together to enable facile CO₂ photoreduction.

### 4.2 Methodology

We ran all DFT calculations with the CP2K code [106, 59]. CP2K uses a mixed method involving Gaussian functions and plane waves[107]. The plane wave representation was expanded to a cutoff of 300 Ry, and the valence electrons were represented by double ζ basis sets [108]. Core electrons were treated by Goedecker-Teter-Hutter pseudopotentials [60]. All calculations were spin-polarized and used
the Perdew Burke Ernzerhof (PBE) exchange correlation functional[53]. We also included dispersion corrections through Grimme’s D3 method with Becke-Johnson damping [54, 55]. Due to self-interaction errors of DFT we utilized the DFT+U correction [109, 110] on Ti d orbitals with a U value of 2.5 eV. We chose this value since it gives gap states for a surface with an oxygen vacancy (from projected density of states calculations) about 0.7 eV below the conduction band, similar to the work of Haa and Alexandrova[89] (U = 3.6 eV) and Selçuk and Selloni[111] (U = 2.5 eV). This U value of 2.5 eV has also been suggested by Hu and Metiu[112] for modeling defective TiO$_2$. Similar settings have been used in our previous work [12]. All calculations were sampled using a single k-point at gamma. We performed charge analysis using the DDEC6 method [113, 114]. In our previous work[12] we compared this method to the popular Bader method[115] of charge analysis and found DDEC6 to be comparable.

![Figure 4.1](image)

Figure 4.1: The supercell used in this work, being a (2x4) representation of the anatase (101) surface. The slab had 288 (fully stoichiometric) or 287 (one oxygen vacancy) atoms. Indicated are different atom types and an oxygen vacancy (O$_v$). The subscripts indicate the coordination number of the atoms, e.g., O$_{2c}$ is a two-coordinated oxygen atom. O$_v$ indicates an oxygen vacancy.

TiO$_2$ anatase (101) surfaces were modeled using periodic slabs with three TiO$_2$
bilayers, or a total of six individual layers, as shown in Figure 4.1. The supercell had \( \sim 20 \, \text{Å} \) of vacuum between slabs. The surface lattice vectors were 20.6 Å and 15.1 Å to give a 2x4 supercell (288 atoms). The atoms in the bottom bilayer were fixed at their bulk positions. We modeled two different surfaces, a stoichiometric surface and a surface with one oxygen vacancy. Adsorption energies of species M were found by the following:

\[
\Delta E_{\text{ads-M}} = E_{M/TiO_x} - E_{TiO_x} - E_M. \tag{4.1}
\]

In this equation \( E_M \) is the energy of species M (e.g. Cu atom or \( \text{CO}_2 \)) in vacuum, \( E_{TiO_x} \) is the energy of a titania surface (either stoichiometric or with an oxygen vacancy), and \( E_{M/TiO_x} \) is the energy of the system with species M adsorbed. We performed climbing image nudged elastic band (CI-NEB) calculations [63, 62] to search the minimum energy pathway and determine activation barriers in \( \text{CO}_2 \) dissociation (\( \text{CO}_2^* \rightarrow \text{CO}^* + \text{O}^* \)) between initial and final states. We used at least 10 images for the nudged elastic band calculations. The NEB calculations were converged when the maximum force on the atoms was smaller than 0.05 eV/Å, similar to Selçuk and Selloni[111].

4.3 Results and Discussion

4.3.1 Adsorption of Cu Atoms

We first modeled a Cu atom adsorbed over stoichiometric and reduced (101) surfaces, as summarized in Figure 4.2. We considered several different initial sites, as discussed in the Supporting Information, but the most stable sites are shown. Over the stoichiometric surface the Cu atom preferred a bridge geometry between
two O$_{2c}$ atoms, similar to previous work[49, 47, 12], with Cu-O$_{2c}$ distances of 1.88 Å. The adsorption energy for a Cu atom over the stoichiometric surface (-2.30 eV) agreed very well with the work by Seriani et al. (-2.30 eV)[49] and Alghannam et al. (-2.26 eV)[47]. The calculated charge of the adsorbed Cu atom over the stoichiometric surface (+0.5) was also in agreement with the work of Alghannam et al. (+0.64)[47]. We tested the effect of +U correction on the adsorption energy of Cu (-2.59 eV without +U correction and -2.30 eV with +U correction), and it agreed with our previously reported value (-2.56 eV without +U correction)[12].

For a surface with an oxygen vacancy, we found three stable adsorption modes: Cu in the vacancy, near the vacancy, and far from the vacancy (Figures 4.2b-d). Several initial sites were modeled, as discussed in the Supporting Information. Previous results on metal atom adsorption over reduced TiO$_2$ surfaces with other transition metals, such as Pt and Au[32, 46, 116], were used to help guide our choice of Cu adsorption sites. We found the most stable adsorption site over the reduced surface occurred when Cu filled the oxygen vacancy (Figure 4.2b), with an adsorption energy of -2.23 eV. A slightly lower adsorption energy (-2.12 eV) was found when the Cu atom adsorbed near the vacancy but did not completely occupy it (Figure 4.2c). When the Cu atom was far from the oxygen vacancy, it interacted with the surface in a similar manner as with the stoichiometric surface (Figure 4.2d), giving a com-
parable adsorption energy (-2.26 eV). Our results show that the Cu atoms became positively charged when interacting with O$_2$ atoms (stoichiometric and far from the oxygen vacancy) but negatively charged when in or near the oxygen vacancy. The region around the vacancy is negatively charged due to unpaired electrons left in the surface on nearby Ti atoms upon O removal, and the surface donates this charge to the adsorbed Cu atom. Negative metal atoms adsorbed in an O$_v$ have been reported previously[32, 117, 100], as well as negative copper clusters[118]. All adsorption energies were close to each other (-2.12 to -2.30 eV), indicating that all geometries could occur upon Cu adsorption over TiO$_2$ and may be catalytically relevant. We thus considered all four geometries when modeling CO$_2$ adsorption and reduction over Cu/TiO$_2$ surfaces.

Our surface model (lone Cu atoms on the TiO$_2$ surface with O$_v$) is commensurate with Cu/TiO$_2$ systems synthesized in experiments. We have shown in previous work[29] that atomic Cu species can be deposited on the TiO$_2$ surface which can lead to CO$_2$ photocatalytic activity. In our other work[12], we demonstrated that single Cu atoms are also stable on the TiO$_2$ surface, while Cu dimers are unstable. Slow diffusion of supported Cu atoms may also limit the formation of dimers and larger clusters[12]. Later (Section 3.5) we discuss how we have synthesized atomic Cu catalysts over reduced surfaces. Finally we note that O$_v$ on the TiO$_2$ can be created through a number of ways, such as annealing[119], doping[120], other treatments[121, 122], or synthesis conditions[123].

In Figure 4.3 is shown the density of states (DOS) for Cu adsorbed on the various surfaces. DOS for the stoichiometric (Figure 4.3a) and reduced TiO$_2$ surfaces (Figure 4.3b) are also given for comparison. A gap state for a surface with O$_v$ was observed due to electrons localizing on Ti atoms, and is a well-known phenomenon. For Cu over TiO$_2$ (Figure 4.3c), a gap state created by Cu was also observed. Similar
gap states have been seen by other authors\cite{33, 100}. For instance, Yang et al.\cite{33} observed gap states for Ag (one row below Cu) clusters in O\textsubscript{v} to be near -1.2 eV and -1.8 eV below the edge of the conduction band.

For Cu in an O\textsubscript{v} a similar gap state due to Cu occurs (near -1.5 eV), but there is also a gap state on TiO\textsubscript{2} due to the O\textsubscript{v} near -0.7 eV which is composed of Ti electrons. Overlap between the Cu and TiO\textsubscript{2} gap states suggest strong interactions, such as Cu in an O\textsubscript{v} (\(~\sim 0.7\) eV) and Cu near an O\textsubscript{v} (between -0.4 eV to 0 eV).

Indeed electron transfer occurs from the O\textsubscript{v} to Cu, with Cu having a -0.35 charge when in the O\textsubscript{v}. When an O\textsubscript{v} forms two unpaired electrons are left in TiO\textsubscript{2} (\(O^{2-} \rightarrow O\textsubscript{v} + \frac{1}{2}O_2 + 2e^-\)) which may reduce two Ti atoms. The two reduced Ti atoms near the O\textsubscript{v} had charges of 1.93 e\textsuperscript{-} and 1.83 e\textsuperscript{-}, compared to the average charge of 2.42 e\textsuperscript{-} for the other Ti atoms. After Cu adsorbed in an O\textsubscript{v}, one of the reduced Ti atoms had a charge of 2.19 e\textsuperscript{-} while the other reduced Ti atom had a charge of 1.73 e\textsuperscript{-}, indicating a net transfer of electrons to the Cu atom from the two Ti atoms. After the charge transfer occurred from TiO\textsubscript{2} to Cu, the O\textsubscript{v} gap states hybridized with the Cu states, as shown in Figure 4.3d and e. For Cu far from an O\textsubscript{v} both gap states for Cu and TiO\textsubscript{2} are seen, but since the Cu does not interact with the O\textsubscript{v}, these states are largely independent of each other and have little overlap.
Figure 4.3: Projected density of states plots for adsorbed Cu. The zero energy level is set at the conduction band edge. The filled curves represent occupied states, while unfilled curves represent unoccupied states.

An important consideration is the effect of adsorbed Cu atoms on the reduction of the TiO\textsubscript{2} surface, for instance through O\textsubscript{2c} removal. It is possible that adsorbed Cu may facilitate or influence the formation of O\textsubscript{v}. The formation energy of an O\textsubscript{v} (O\textsubscript{2c} \rightarrow O\textsubscript{v} + \frac{1}{2}O\textsubscript{2}) for TiO\textsubscript{2} was found to be 4.43 eV, similar to the value by Cheng et al. (4.34 eV)\cite{84}. However, we calculated the O\textsubscript{v} formation energy in the presence of Cu (or starting with a Cu/TiO\textsubscript{2} surface) to be between 4.47 and 4.61 eV, depending on whether the Cu atom in the final state was in the O\textsubscript{v}, near the O\textsubscript{v}, or far from the O\textsubscript{v}. These energies indicate that Cu is not likely to help increase the number of O\textsubscript{v}. Rather O\textsubscript{v} on the surface could form by other means.
4.3.2 Adsorption of CO$_2$

Figure 4.4: Summary of CO$_2$ adsorption over TiO$_2$ and Cu/TiO$_2$. (a) The adsorption energies of CO$_2$ of the most stable linear and bent configurations are given. (b) The calculated charges of the most stable adsorbed CO$_2$ are also shown. Geometries for the most stable bent configurations are given in Figure 4.5.

We modeled CO$_2$ adsorption over the various TiO$_2$ and Cu/TiO$_2$ surfaces. Formation of bent CO$_2$ is a key step in CO$_2$ activation in order to further reduce the
Figure 4.5: Most stable bent CO$_2$ adsorption geometries over TiO$_2$ and Cu/TiO$_2$ surfaces. Shown is CO$_2$ adsorption over several surfaces: a stoichiometric surface (S1), a stoichiometric surface with a Cu adatom (S2), a reduced surface with oxygen vacancy (R1), a reduced surface with a Cu adatom in an oxygen vacancy (R2), a surface with Cu near an oxygen vacancy (R3), and a surface with Cu far from the oxygen vacancy (R4). The CO$_2$ adsorption energies are given.

molecule[124, 5]. Linear CO$_2$ is inert and resistant to reactivity. We have summarized results for both linear and bent CO$_2$ adsorption in Figure 4.4, giving both adsorption energies and calculated charges of CO$_2$. We modeled CO$_2$ adsorption over stoichiometric surfaces (configurations S1 and S2), and reduced surfaces (configurations R1-R4). Figure 4.5 shows the final optimized geometries for bent CO$_2$. Figure A.3 shows the adsorbed linear CO$_2$ geometries, while Figure A.4 shows other less stable bent configurations that we found.

Over stoichiometric TiO$_2$ (configurations S1 and S2), linear CO$_2$ adsorption was more stable than bent CO$_2$, regardless of whether Cu is present. The linear and bent CO$_2$ energies on TiO$_2$ (-0.20 eV for bent and -0.39 eV for linear) and Cu/TiO$_2$ (-0.28 eV for bent and -0.37 eV linear) are in agreement with our previous work[12]. Linear CO$_2$ had charges near 0 e$^-$ (see Figure 4.4b) while bent CO$_2$ had negative charges near -0.3 e$^-$ over stoichiometric TiO$_2$. Stoichiometric TiO$_2$ has no free electrons available to readily transfer to CO$_2$ which could explain why neutral, linear CO$_2$ is more stable than the bent, anionic CO$_2$ over the stoichiometric surface. Electron transfer from the Cu/TiO$_2$ surface to CO$_2$ was also apparently difficult, at least
compared to the reduced surfaces as discussed below. This leads to linear CO$_2$ being more stable than bent CO$_2$ over the two stoichiometric surfaces we modeled. We note that the bent CO$_2$ configuration over the stoichiometric surface (see configuration S1 in Figure 4.5) resembled a carbonate-like structure, which was also observed in previous work [34, 5, 12].

We next analyzed the effect of surface vacancies on CO$_2$ adsorption. Bent CO$_2$ is markedly stabilized over the surfaces with O$_v$ present, as Figure 4.4 and Figure 4.5 show. Over TiO$_2$, the O$_v$ leads to a very strong bent CO$_2$ structure, as the CO$_2$ molecule fills the O$_v$ (see R1 in Figure 4.5). The adsorption energy of bent CO$_2$ in an O$_v$ was -1.28 eV, compared to linear CO$_2$ having an adsorption energy of -0.85 eV. We also compared our adsorption energies to literature papers that modeled the TiO$_2$ anatase (101) with O$_v$ and adsorbed bent CO$_2$. Sorescu et al. [34] reported an adsorption energy of -1.35 eV for the R1 case, which is similar to our adsorption energy of -1.28 eV. He et al. [5] reported an adsorption energy of -1.09 eV for the R1 configuration at the PBE level, similar to our calculated PBE value of -0.92 eV. He et al. used a (2 x 1) TiO$_2$ surface cell whereas our work using a larger (2 x 4) surface cell, which might explain the slight differences. Further details on the effect of the +U correction can be found in the Supporting Information.

When Cu is present on a reduced surface, we observed strong stabilization of bent CO$_2$, with bent CO$_2$ adsorption energies of -0.85 eV (R2), -1.30 eV (R3), and -1.29 eV (R4). Interestingly, the bent CO$_2$ adsorption energies over a surface with O$_v$ (R1) and Cu/O$_v$ (R3) are comparable. In all cases over reduced surfaces bent CO$_2$ is preferred over linear CO$_2$, but for the R2, R3 and R4 states this preference is very pronounced, with energy differences of -0.34, -1.03 eV and -0.80 eV, respectively, between the linear and bent CO$_2$ structures. Such significant differences in adsorption energies between linear and bent CO$_2$ suggest high selectivity for bent
CO₂ formation over surfaces with both Cu and Oₙ present, and hence potentially larger CO₂ reduction activity.

Bent CO₂ had O-C-O angles near 130° (see Table A.1) while linear CO₂ angles were all near 180°, indicating the activated nature of CO₂. In the R1 configuration, CO₂ had all three atoms (O, C, O) bonding with the Ti near the oxygen vacancy. The R4 configuration had essentially the same CO₂ bent adsorption energy and structure as R1, suggesting that the Cu adatom in R4 was far enough from the Oₙ so that it did not interact with the adsorbed CO₂ or Oₙ significantly.

In the R2 configuration, the Cu adatom bound to the Oₙ strongly and blocked the CO₂ molecule from filling the Oₙ. The CO₂ bent as it formed bonds (Cu-C and Ti-O) with the surface. In the R3 configuration, the optimized bent CO₂ structures appeared to be very similar to R2 configuration (see Figure 4.5). CO₂ only had two atoms (O and C) bonding with the surface in the R2 and R3 configurations: one O atom of the CO₂ bound to the Ti atom near the Oₙ and the C atom interacted with two Ti atoms. The CO₂ charge in the R2 configuration was -0.56 e⁻ for instance, while in the R3 configuration the CO₂ charge was -0.63 e⁻. Their adsorption energies were however different, with the R3 configuration being 0.45 eV more stable than the R2 geometry. The Cu atom in the R3 configuration was further from the Oₙ which allowed Cu interactions with the surface O₂c atom. In the bent CO₂ R2 configuration, the Cu atom was 1.23 Å from the Oₙ site, while in the R3 configuration the Cu atom was 1.48 Å from the Oₙ site. This slightly different configuration could lead to the R3 configuration being more stable than R2 configuration. We further examined the stability of the R2 site by perturbing the Cu atom away from the Oₙ and allowing geometry optimization. We found that with sufficient perturbation the R2 configuration relaxed to the R3 configuration, which suggests that R2 may be a local minimum.
O\(_v\) should be highly reactive due to under-coordinated surface atoms, but may also generate excess electrons which may transfer to the CO\(_2\) molecule, as shown in previous work [30, 125]. Figure 4.4b shows that all the bent CO\(_2\) became very negative when O\(_v\) was present, being -0.28 e\(^-\) (S1) and -0.35 e\(^-\) (S2) over stoichiometric surfaces while -0.74 e\(^-\) (R1), -0.56 e\(^-\) (R2), -0.63 e\(^-\) (R3), and -0.74 e\(^-\) (R4) over the reduced surfaces. All the linear CO\(_2\) had similar charges, being slightly cationic, near 0 e\(^-\). The most negatively charged CO\(_2\) occurred in the R1 and R4 configurations (-0.74 e\(^-\)), where both O atoms of CO\(_2\) formed bonds with nearby Ti atoms. In both the R1 and R4 configurations, one reduced Ti atom (adjacent to the adsorbed CO\(_2\)) lost 0.36 e\(^-\) and the other gained 0.1 e\(^-\) upon CO\(_2\) adsorption. Likewise, CO\(_2\) gained 0.37 e\(^-\) while the C atom was nearly neutral after adsorption. When only one O atom and the C atom of CO\(_2\) interacted with surface Ti and Cu atoms, as observed as in the R2 and R3 cases, the calculated charges on CO\(_2\) were -0.56 e\(^-\) and -0.63 e\(^-\), respectively. In R3 for example, the C had a charge of +0.28 e\(^-\), while the O atoms had charges of -0.35 e\(^-\) (O away from the surface) and -0.57 e\(^-\) (O close to the surface) after CO\(_2\) adsorption. However, despite having less CO\(_2\) charge, the R3 configuration had almost the same adsorption energy as R1 and R4, which had more negative CO\(_2\) charge, suggesting that the presence of the Cu adatom in R3 had a substantial effect in stabilizing bent CO\(_2\).
Projected density of states details for adsorbed bent CO$_2$ are shown in Figure 4.6. For the S1 configuration, the majority of CO$_2$ bands are near the edge of the valence band (-2 eV below the conduction band), which is 2 eV higher than the CO$_2$ bands in the gas phase which has a characteristic peak near -4 eV below the conduction band (shown in Figure A.6). For the S2 configuration, the Cu state overlapped with the TiO$_2$ states, while overlap of Cu and CO$_2$ states were minimal, suggesting stronger Cu/TiO$_2$ and weaker Cu-CO$_2$ interactions. This agrees with the previous work by Iyemperumal and Deskins [12]. For the R1 configuration, the highest CO$_2$ energy level was near -1.7 eV. The gap state created by the oxygen vacancy (shown in Figure 4.3b) also shifted to near -1.7 eV in the R1 configuration (Figure 4.6c). Charge transfer from the reduced Ti atoms to CO$_2$ and interactions between the CO$_2$ molecule and nearby Ti atoms occurred. Charge analysis showed that the one of the Ti$^{3+}$ atoms lost 0.26 e$^-$ and the other gained 0.10 e$^-$ after CO$_2$ adsorption to have charges of 2.19 and 1.73, which brought one of the Ti atoms to a Ti$^{4+}$ state.
(near 2.31 e\(^-\)). The one Ti\(^{3+}\) state shifted to near -1.7 eV and completely overlapped with the CO\(_2\) band. Despite a net charge transfer from the Ti\(^{3+}\) to bent CO\(_2\), other surface atoms also donated charge to CO\(_2\) (leading to a final CO\(_2\) charge of -0.74 e\(^-\)). In the R2 and R3 cases (Cu in and near O\(_v\)), Cu bands were in the valence band region, while a portion of the CO\(_2\) states were at higher energies near the edge of the conduction band. These CO\(_2\) bands hybridized very well with gap states of TiO\(_2\) and Cu states, indicating strong interactions between CO\(_2\) and Cu/O\(_v\) surface.

4.3.3 CO\(_2\) Reactivity

We already demonstrated how activation of CO\(_2\) to its bent structure occurs when Cu atoms and O\(_v\) are present. We now discuss the reactivity of CO\(_2\) over the various TiO\(_2\) surfaces. Using the CI-NEB method we calculated several barriers for CO\(_2\) dissociation over select surfaces. Formation of CO from CO\(_2\) is one of the proposed early steps of CO\(_2\) reduction[88, 103], with subsequent hydrogenation steps forming various intermediates and products. In Table 4.1 we summarize the calculated reaction energies and activation barriers for the reaction CO\(_2^*\) → CO\(^*\) + O\(^*\). We started with bent CO\(_2\) in all cases, and details on CO and O adsorption can be found in the Supporting Information. For the stoichiometric surface (S1) the CO\(_2\) dissociation energy was found to be 1.50 eV. Since the reaction energy was so large, we expect the activation barrier to be at least 1.50 eV, and did not calculate the activation barrier. Over the Cu/TiO\(_2\) surface (S2) the dissociation energy was 0.58 eV. We calculated the activation barrier to be 0.83 eV for the Cu/TiO\(_2\) case (S2). Thus, it appears that CO\(_2\) dissociation over these stoichiometric surfaces is likely to proceed at a very slow rate since the activation barriers prevent rapid CO\(_2\) dissociation and reduction. The dissociation path for the S2 configuration can be found in Figure A.8a in the Supporting Information.
Table 4.1: Summary of reaction energies and select activation barriers for bent CO$_2$ dissociation, CO$_2^* \rightarrow$ CO$^*$ + O$^*$. All numbers are in eV.

<table>
<thead>
<tr>
<th>Site</th>
<th>S1</th>
<th>S2</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.50</td>
<td>0.58</td>
<td>-0.40</td>
<td>-1.71</td>
<td>-1.36</td>
<td>-0.30</td>
</tr>
<tr>
<td>Reaction Energy</td>
<td>&gt;1.50 eV</td>
<td>0.83</td>
<td>0.95</td>
<td>0.10</td>
<td>0.19</td>
<td>0.95</td>
</tr>
<tr>
<td>Cu + e-</td>
<td>1.39</td>
<td>-0.50</td>
<td>-0.42</td>
<td>-1.44</td>
<td>-1.17</td>
<td>-0.39</td>
</tr>
<tr>
<td>Reaction Energy</td>
<td>&gt;1.39 eV</td>
<td>0.57</td>
<td>0.97</td>
<td>0.19</td>
<td>0.27</td>
<td>0.97</td>
</tr>
<tr>
<td>Pt</td>
<td>1.50</td>
<td>-0.21</td>
<td>-0.40</td>
<td>-1.08</td>
<td>-1.13</td>
<td>-0.39</td>
</tr>
<tr>
<td>Reaction Energy</td>
<td>&gt;1.50 eV</td>
<td>0.85</td>
<td>0.95</td>
<td>0.43</td>
<td>0.46</td>
<td>0.95</td>
</tr>
</tbody>
</table>

We also modeled CO$_2$ dissociation over reduced surfaces. The calculated dissociation energy of CO$_2$ in an O$_v$ (configuration R1) was -0.40 eV, and the barrier was 0.95 eV. Sorescu et al.[34] reported an activation barrier of 0.90 eV for CO$_2$ dissociation over O$_v$/TiO$_2$, while Ji and Luo[88] found a barrier of 0.73 eV. Our calculated activation barrier was comparable to these literature results. We expect that for Cu far from the O$_v$ (R4) the activation barrier will be similar to R1, given their similar adsorption energies, geometries, and dissociation energies. The effect of single metal atoms and O$_v$ on CO$_2$ reactivity is unknown, and we applied the CI-NEB method to calculate activation barriers for CO$_2$ dissociation starting with the R2 and R3 configurations. Figure 4.7 shows the two pathways for CO$_2$ dissociation over these surfaces. In both cases, the CO$_2$ dissociates to fill the O$_v$ and pushes the Cu out or away from the O$_v$. The barriers are very low in both cases. For the R2 configuration, the process is energetically downhill with a small activation barrier of 0.1 eV (energy from the local minimum in image 3 to image 4). If the energy is not fully dissipated to the surrounding surface as the CO$_2$ molecule transitions from im-
age 1 to the lower energy image 3 state, then CO$_2$ dissociation may be barrier-less. The R3 configuration has an activation barrier of only 0.19 eV. Both the R2 and R3 dissociation pathways are similar. But the R2 configuration, as we discussed in Section 3.2, was less stable than the R3 configuration. This corresponds to a dip in the energy path from image 1 to 3 (shown in Figure 4.7a) where the CO$_2$ molecule reaches a state similar to the R3 configuration. The slightly different geometry contributes to the difference in the activation barrier of 0.09 eV between the R2 and R3 cases.

Figure 4.7: The calculated climbing image nudged elastic band pathways for CO$_2$ dissociation over (a) Cu in an O$_v$ (R2) and (b) Cu near an O$_v$ (R3).

These results show that a single Cu atom and O$_v$ lowers the barrier for CO$_2$
reactivity substantially compared to just stoichiometric or reduced TiO$_2$ surfaces or Cu/TiO$_2$. Importantly, our work confirms experimental work, where it was shown that Cu and O$_v$ could lead to spontaneous CO$_2$ dissociation even under dark conditions. Liu et al.[13, 14] observed experimentally that CO$_2$ species spontaneously dissociated into CO even in the dark on a reduced Cu/TiO$_2$ surface. In their proposed CO$_2$ dissociation mechanism CO$_2$ dissociated and healed the oxygen vacancy and formed a Cu-CO complex. Our CI-NEB results confirm this mechanism as we have shown the activation barrier is very low and promotes CO$_2$ dissociation significantly. The oxygen vacancy is healed as Figure 4.7 indicates.

Our results show that CO$_2$ dissociation in an O$_v$ has a high barrier (at least 1.5 eV), while dissociation in or near Cu/O$_v$ is much smaller (< 0.2 eV). The role of Cu can be further understood by analyzing the CO$_2$ charges and geometries. In the R1 case, where CO$_2$ filled the O$_v$, the surface excess electrons transferred to both O atoms. The O atoms in CO$_2$ had charges of -0.37 e$^-$, while the carbon remained neutral. Analysis of the TiO$_2$ charges indicates that these electrons on O came predominantly from reduced Ti atoms. However, in the case of Cu near O$_v$ (R3) the O atom in CO$_2$ that interacted with the surface had a charge of -0.57 e$^-$, while the other O atom had a charge of -0.35 e$^-$. The C atom in the R3 case had a charge of +0.28 e$^-$. Furthermore the CO$_2$ charge distributions in R1 and R3 also mirrored the C-O bond distances. The CO$_2$ in R1 was symmetric with C-O bond distances of 1.26 Å, while the CO$_2$ in R3 had C-O bond distances of 1.22 Å and 1.33 Å (summarized in Table A.1). The O atom that interacted with Ti in R3 had an elongated C-O bond compared to R1, indicating that this molecule could be in a pre-activated state. Indeed, the activation barrier to break this bond is much lower for R3 compared to R1, as our CI-NEB calculations show.
4.3.4 The Effect of Photoexcited Electrons

Figure 4.8: Adsorption energies of (a) Cu adatoms and (b) bent CO$_2$ over various surfaces in the presence of an extra electron. The extra electron was modeled using a hydrogen atom, similar to the work of He et al.[5]

In order to analyze the possible effect of photoexcited electrons, we modeled both Cu and CO$_2$ adsorption in the presence of an unpaired electron, similar to the method used by He et al.[5] A hydrogen atom was placed on the surface, away from the CO$_2$
adsorption site, and served to donate an electron to the surface. Models with extra net charge, rather than hydrogen atom as an electron donor, performed similarly in modeling an extra electron[5]. This extra electron could transfer to adsorbates and served to mimic a photoexcited electron. Figure 4.8a shows adsorption energies of Cu atoms when such an electron was present compared to the case of no extra electron present, and Figure 4.8b shows similar results for adsorption of bent CO$_2$. For Cu on the stoichiometric surface or away from the O$_v$, the adsorption energy either did not change or was slightly destabilized by 0.1 eV. In the presence of an extra electron the Cu binding to TiO$_2$ with O$_v$ was strengthened by 0.43 eV (R2) and 0.44 eV (R3). Since the Cu atom was more stabilized in an O$_v$ when an excited electron was present, this may favor the migration or adsorption of Cu atoms into O$_v$ sites under photocatalytic conditions. The charges of the Cu atoms in Figure 4.8a can be found in Table A.2 in the Supporting Information. We also modeled the effect of photoexcited electrons on linear CO$_2$ adsorption as summarized in Figure A.10. We found the adsorption trends were the same compared to the no extra electron case, in that bent CO$_2$ was preferred over the reduced surfaces and linear CO$_2$ was preferred stoichiometric surfaces. The linear CO$_2$ adsorption energy for Cu in an O$_v$ (R2) and for Cu near an O$_v$ became more exothermic by 0.31 eV and 0.07 eV, respectively, in the presence of an extra electron. Other linear CO$_2$ adsorption energies did not change in the presence of the extra electron.

For bent CO$_2$ adsorption in every case (except over stoichiometric TiO$_2$) the adsorption energies became stronger when an extra electron was present (see Figure 4.8b). The adsorption energies became more negative by 0.05 to 0.28 eV. We calculated the charges of CO$_2$ over the surfaces with an unpaired electron present, and summarize them in Table A.3. We found that the charges of CO$_2$ did not change significantly when the electron was present. Since the charges of bent CO$_2$
were the same regardless of whether an unpaired electron was present, we attribute the stronger adsorption energies to the ease of electron transfer from the surface to CO₂. There is an energy cost for removing charge from the surface to the CO₂ molecule, and when an extra electron is present, this cost is diminished. The extra electron more readily transfers to CO₂ compared to the surface without an electron present. These results suggest that photoexcited electrons, along with Cu atoms and Oᵥ, may further stabilize activated, bent CO₂ and lead to efficient CO₂ photo-reduction.

We also modeled CO₂ dissociation in the presence of the unpaired electron. Results are shown in Table 4.1. Over stoichiometric TiO₂ (S1) the presence of the electron had a slight effect and the reaction energy was more exothermic by 0.11 eV, but overall the reaction was still quite endothermic at 1.39 eV. In the case of Cu/TiO₂ (S2) the effect was quite dramatic. The reaction energy dropped by 1.08 eV and becomes -0.50 eV, which is reasonably exothermic. Further NEB modeling of this reaction gave a barrier of 0.49 eV (see Figure A.8 for NEB pathways), which indicates that photoexcited electrons may very strongly enable CO₂ adsorption and reactivity over Cu/TiO₂. For the reduced surfaces where Cu did not interact with the CO₂ molecule (R1 and R4), the extra electron did not change the reaction energies significantly. The calculated reaction barriers with an photoexcited electron for Cu in an Oᵥ (R2) and Cu near an Oᵥ (R3) were 0.09 eV and 0.08 eV higher than barriers with no extra electron, indicating this extra electron did not have a positive role in dissociating CO₂ like for other cases (e.g. S2 or Cu/TiO₂). The photoexcited electron therefore had a more substantial effect for CO₂ dissociation on Cu/TiO₂ (S2) than on Oᵥ (R1) and Cu/Oᵥ (R2,R3). The reduced surfaces already had unpaired electrons, so further unpaired electrons did not improve CO₂ dissociation kinetics.
4.3.5 Experimental Results on CO$_2$ Activation and O$_v$

In Appendix B we have provided details on experiments performed by the groups of Professor Gonghu Li at the University of New Hampshire and Professor Ronald Grimm at Worcester Polytechnic Institute. The work shows that bent CO$_2$ formed over Cu/TiO$_2$ samples with measured adsorption intensities being Cu/O$_v$/TiO$_2$ > O$_v$/TiO$_2$ > Cu/TiO$_2$ > TiO$_2$, in agreement with our DFT calculations. Photocatalytic studies also indicate CO$_2$ dissociation to form CO occurs with detected product amounts following these trends: Cu/O$_v$/TiO$_2$ > Cu/TiO$_2$ > O$_v$/TiO$_2$. These experimental results suggest that O$_v$ and Cu may increase CO$_2$ reduction activity, just as our modeling shows.

4.3.6 Pt/TiO$_2$, and CO$_2$ Reduction

While we have focused on Cu/TiO$_2$ catalysts, we also briefly consider Pt atoms adsorbed on TiO$_2$. Pt is a prototypical catalyst and has been studied for CO$_2$ reduction using small clusters[33, 101, 45, 126, 102]. Our analysis could provide insight on how different metals may perform as supported single atom catalysts for CO$_2$ reduction. In Figure 4.9a, the adsorption energies of Pt are shown over stoichiometric and reduced surfaces, as well as for comparison results of Cu. Corresponding geometries can be found in Figure A.15. Pt atoms bound substantially stronger to all of the four sites compared to Cu. The Pt adsorption energy over the stoichiometric surface was -3.3 eV, while the adsorption energy was -5.4 eV for Pt in an O$_v$ and Pt near the O$_v$, and -3.1 eV for Pt away from an O$_v$. Similar results were obtained by Gong et al.[32] who reported an adsorption energy of -4.71 eV for Pt in an O$_v$. Our calculations were at the PBE+D3+U level, while Gong et al. used PBE only, which could explain the slight difference in adsorption energies. In any
case, Pt binds much stronger to the surface than Cu.

Since Pt interacts differently than Cu with the TiO$_2$ surface, it could influence the formation of O$_v$ differently than Cu. We found Cu to have no real effect on O$_v$ formation (see Section 3.1). In contrast, the O$_v$ formation energy decreased by 2.13 eV and 2.24 eV when a Pt atom was present in/near O$_v$ respectively, and increased by 0.13 eV when Pt was away from O$_v$ (similar to the case of Cu away from the O$_v$). This indicates that Pt could potentially increase the number of O$_v$, which may have a strong effect on surface reactivity.
Figure 4.9: Results from modeling Pt/TiO₂ surfaces. (a) Adsorption energies of Pt adatoms compared to Cu adatoms. (b) Adsorption energies of bent and linear CO₂ over Pt/TiO₂ surfaces.

In Figure 4.9b, we give the adsorption energies of linear and bent CO₂. In contrast to Cu, over the stoichiometric surface with Pt (S2) bent CO₂ was preferred over linear CO₂ by 0.21 eV. Notice also that for Pt, the S2 configuration has a close adsorption energy (near -0.64 eV) to that of the R2 and R3 configurations,
indicating that Pt/O_v did not promote CO_2 activation as well as Cu/O_v did. Over the Pt/reduced TiO_2 surfaces, the bent CO_2 binding geometries to the surface (R2, R3, R4 configuration) are nearly identical to the Cu case (see Figure A.15). The bent CO_2 adsorbed more strongly (in the range of 0.38 eV to 0.53 eV) than linear CO_2, which was the same trend we observed for the Cu/reduced TiO_2 case. However, comparing Pt and Cu, bent CO_2 in the R2 and R3 configurations was more strongly bound over Cu/TiO_2 compared to Pt/TiO_2. This difference could be a result of the Pt charges (negative), where Pt was -0.51 e^- and Cu was +0.02 e^- for the R2 case. The two anions (Pt and CO_2) could have more repulsion compared to the Cu/O_v/TiO_2 case, since Cu was positively charged, leading to stronger CO_2 adsorption over Cu/O_v/TiO_2.

We also considered CO_2 reactivity over Pt/TiO_2 surfaces. Table 4.1 contains a summary of CO_2 dissociation energies for Pt over TiO_2. The reaction energy for dissociation of CO_2 was exothermic for the Pt/TiO_2 (S2) case compared to an endothermic reaction energy for Cu/TiO_2. However, the activation energies over Pt and Cu were nearly the same over these catalysts, being 0.83 eV (Cu-S2) and 0.85 (Pt-S2). When Pt was in the O_v (R2) the CO_2 dissociation energy was -1.08 eV, which was less exothermic than the Cu-R2 case (-1.71 eV ). The dissociation barrier was 0.43 eV, which is about twice the barrier for the Cu case (0.19 eV). The Pt-R2 and Pt-R3 configurations had similar reaction energies and activation barriers due to the similarity in geometries. These results show that Pt over stoichiometric surfaces may be a more promising catalyst compared to Cu, but that the strong synergy between metal atom and O_v is largely absent for Pt, while such strong synergy occurs for Cu. In this work, we did not model Pt/TiO_2 with photoexcited electrons. However, in recent work by Yang et al.[102], a Pt tetramer with multiple photoexcited electrons on a TiO_2 surface was shown to have a lowered barrier for
Figure 4.10: A summary of possible CO$_2$ dissociation pathways as calculated by DFT. Given are reaction and activation energies. The dotted line suggests a "cut-off" activation energy (< 0.6 eV), where activation energies below this line are expected to proceed reasonably fast. Several surfaces are good catalysts for CO$_2$ reduction: Cu/TiO$_2$ with photoexcited electron, Pt/O$_{v}$/TiO$_2$, Cu/O$_{v}$/TiO$_2$, and Cu/O$_{v}$/TiO$_2$ with photoexcited electron.

CO$_2$ reduction. We therefore could expect that photoexcited electrons could have a stabilizing effect for single Pt atoms, just like for Cu atoms.

4.4 Conclusions

In this work, we systematically investigated the effect of defects and excited electrons on CO$_2$ reduction using TiO$_2$ supported single atom metal photocatalysts. We first found using DFT that Cu binds strongly to both the stoichiometric and reduced TiO$_2$ surfaces, indicating that single site Cu catalysts maybe stable over TiO$_2$. Activation of CO$_2$ occurs as bent CO$_2$ forms from the linear CO$_2$ structure. Cu atoms in/near an oxygen vacancy were highly selective towards bent CO$_2$ CO$_2$ formation, in contrast to Cu over stoichiometric TiO$_2$. Furthermore, the Cu/O$_{v}$ complex can lower the reaction barrier for CO$_2$ dissociation (CO$_2^* \rightarrow$ CO$^*$ + O$^*$)
to very low values (0.10 - 0.19 eV), which gives high catalytic production of CO. This spontaneous dissociation of CO$_2$ also agrees with experimental results[13, 14]. Our own experimental work showed that bent CO$_2$ formed over Cu/TiO$_2$ samples with measured adsorption intensities of Cu/O$_{v}$/TiO$_2$ > O$_{v}$/TiO$_2$ > Cu/TiO$_2$ > TiO$_2$, in agreement with our theoretical calculations. Our photochemical studies also indicate CO$_2$ dissociation most readily occurs on Cu/O$_{v}$/TiO$_2$ surfaces.

We also confirmed that a photoexcited electron may be beneficial in stabilizing bent CO$_2$ on both Cu/TiO$_2$ and Cu/O$_{v}$ surfaces. Significant decreases in the reaction energy (∼1 eV) and barrier (0.26 eV) were calculated when an electron was present for Cu over stoichiometric TiO$_2$. Such an effect was not observed over reduced surfaces since such surfaces already had unpaired electron(s) present. These results imply that photocatalytic activity over activity over Cu/TiO$_2$ should be higher than thermal catalytic activity, and details the direct role of photoexcited electrons in reducing CO$_2$. We also modeled Pt as an alternative to Cu, and found that Pt bound much stronger to TiO$_2$ than Cu. Pt/O$_{v}$ also showed selectivity to adsorbed bent CO$_2$ over linear CO$_2$, which was similar to Cu/O$_{v}$. Reaction barriers for CO$_2$ dissociation were low for the Pt/O$_{v}$ surface (0.43 eV), although the strong synergy for Cu/O$_{v}$ (reaction barriers 0.1 to 0.19 eV) was not observed. We have summarized our calculated reaction results in Figure 4.10. This figure shows that several catalysts may enable facile reduction of CO$_2$, and that O$_{v}$ and photoexcited electrons may assist single atoms significantly in this process. Our work on single atomic catalysts for CO$_2$ reduction highlights promising ways to tailor the catalyst, such as controlling surface defects or increasing photoexcitation yield, and further motivates research on a variety of supported single atom photocatalysts.
Chapter 5

Conclusions and Recommendations

In the thesis, we systematically investigated the effect of defects and excited electrons on CO₂ reduction using TiO₂ supported single atom metal photocatalysts. Our work highlights promising ways to tailor the catalyst, such as controlling surface defects or increasing photoexcitation yield, and further motivates research on a variety of supported single atom photocatalysts. We have found that Cu atoms with O_v aid in the process of bent, anionic CO₂ formation and lowered the activation barrier for CO₂ dissociation to 0.10 - 0.19 eV, which could enable fast reduction of CO₂ even at room temperature, in agreement with experimental findings. A photoexcited electron was shown to readily promote Cu binding to the surface vacancy, and CO₂ adsorption and dissociation. Finally we found, similar to Cu, that a single Pt with O_v can promote CO₂ dissociation. Future work may include the study of Pt/TiO₂ or other metals with photoexcited electrons. In recent work by Yang et al.[102], a Pt tetramer with multiple photoexcited electrons on a TiO₂ surface was shown to have a lowered barrier for CO₂ reduction. We therefore could expect that
photoexcited electrons could have a stabilizing effect for single Pt atoms, just like for Cu atoms. A similar approach could also address the effect of multiple photoexcited electrons on other supported single metal atoms. For surface defects, we now have some understanding of how Cu/O\textsubscript{v} and Pt/O\textsubscript{v} can aid in CO\textsubscript{2} reduction; future work could investigate the effect O\textsubscript{v} and other single atoms (Co, Ni, etc.) in CO\textsubscript{2} reduction. Besides surface defects, other types of defects can play important role in CO\textsubscript{2} reduction. There are several reports[84, 127, 128] showing sub-surface defects that can affect adsorption of CO\textsubscript{2} at the surface, and studies of these defects may also be an important area of research for CO\textsubscript{2} reduction over supported metal atoms. Other metal oxide supports could be studied in order to understand if the synergy between O\textsubscript{v} and photoexcited electrons exists for metal atom catalysts over other supports. Our work shows how theory can be used to understand surface features of photocatalysts and predict which features may be important in accelerating CO\textsubscript{2} reduction. Single atom catalysts show promise and may eventually lead to carbon-neutral energy.
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[64] Nudged Elastic Band Transition State Tools for VASP.


Appendix A

Supporting Information
Figure A.1: Cu was placed at various initial positions, as indicated, on a stoichiometric anatase (101) surface. Symmetrically equivalent sites are not shown in the upper half of the image. Position 7 represents the Cu between the two-coordinated oxygens (O$_{2c}$), which was the most stable geometry. Red spheres represent O atoms, while blue spheres represent Ti atoms.

Figure A.1 shows the various sites over the stoichiometric surface where we modeled Cu adsorption. We modeled metal adsorption on top of Ti and O atoms, such as position number 2, 3, 4 etc., as well as in "hollow" sites, such as position number 1, 5 and 7. Only the most stable geometry (site 7) was discussed in the main paper. Previous work[49, 47, 12] identified that Cu adatom was most stable at the bridge site between the two O$_{2c}$ atoms, as verified in our own work.
A.2 Cu Adsorption over Reduced TiO$_2$

Figure A.2: Cu was placed at various initial positions, as indicated, on an anatase (101) surface with an O$_V$. Symmetrically equivalent sites are not shown in the lower half of the image. Position 1 represents the Cu in the O$_V$, which was the most stable geometry. Red spheres represent O atoms, while blue spheres represent Ti atoms.

Figure A.2 shows the various sites over the reduced surface where we modeled Cu adsorption. We modeled metal adsorption on top of Ti and O atoms, such as position number 2, 3, 4 etc., as well as in "hollow" sites, such as position number 8, 10 - 13. Only a few select geometries were found to be stable and are discussed in the main paper. Previous work[32, 46, 116] identified that a metal atom (such as Au and Pt) was most stable in an O$_V$, similar to our own work.
A.3 Linear CO$_2$ Adsorption

Figure A.3: Final linear CO$_2$ adsorption geometries. Shown is CO$_2$ adsorbed over several surfaces: a stoichiometric surface (S1), a stoichiometric surface with a Cu adatom (S2), a reduced surface with oxygen vacancy (R1), a reduced surface with a Cu adatom in an oxygen vacancy (R2), a surface with Cu near an oxygen vacancy (R3), and a surface with Cu far from the oxygen vacancy (R4). The CO$_2$ adsorption energies are indicated.

Figure A.3 shows the most stable linear CO$_2$ geometries at the six possible surface sites. All the CO$_2$ molecules in Figure A.3, except for R2, have only one oxygen atom interacting with surface atoms. For the linear S1 site, He et al.[5] reported a CO$_2$ adsorption energy of -0.20 eV, which is slightly less stable than our adsorption energy (-0.39 eV). Our calculations however included a dispersion (D3) correction[55].
A.4 Other Stable Bent CO$_2$ over Cu in O$_v$

Figure A.4: An example of four stable bent CO$_2$ optimized geometries interacting with Cu in the oxygen vacancy. CO$_2$ adsorption energies are given above each geometry. All geometries are less stable than those reported in the main text.

We modeled over 60 different CO$_2$ adsorption geometries across the three Cu/O$_v$ sites shown in the main paper. In the main paper we discuss the most stable geometry for each Cu/O$_v$ type. In Figure A.4 we show several other stable CO$_2$ bound to Cu in an O$_v$ (R2). For Cu near an O$_v$ (R3) where bent CO$_2$ did not interact with the O$_v$ directly, the Cu atom tended to fall into the O$_v$, or the R2 geometry. When bent CO$_2$ interacted with O$_v$ directly, the Cu atom still bound O$_v$ stronger than CO$_2$, resulting in the R3 configuration discussed in the main text.
Some of the bent geometries become linear after geometry optimization and vice versa. These geometries are less stable than the most stable geometries that we reported in the main text. All of the geometries here are 0.89 eV to 1.15 eV less stable than the most stable bent CO$_2$ geometry (R3) from the main text which had an adsorption energy of -1.30 eV.

A.5  Effect of +U and Dispersion Corrections on CO$_2$ Adsorption

Figure A.5(a) shows the bent CO$_2$ adsorption energies at three levels of theory: PBE\cite{PBE}, PBE+D3\cite{PBE-D3}, and PBE+D3+U\cite{PBE-D3+U, PBE-D3+U-2} (U = 2.5 eV on Ti). The PBE+D3 calculations took into account dispersion forces and typically gave more negative adsorption energies, from 0.05 to 0.43 eV lower compared to PBE (except for site S1). PBE+D3+U results gave more negative adsorption energies compared to PBE+D3 for the R1, R3, and R4 configurations, in the range of 0.02 to 0.37 eV. Across the three levels of theory the adsorption energies became more stable as we implemented D3 and +U subsequently, except for the R2 case. The PBE+D3+U adsorption energy for the R1 configuration had the most negative adsorption energy, which could be a result of both reduced Ti atoms interacting with the CO$_2$, as the +U method localized the excess electrons in the vicinity of the O$_V$ site. In Figure A.5(b), the spin densities of the reduced TiO$_2$ surface show that the excess electrons were localized on nearby Ti atoms with the +U method while the excess electrons delocalized throughout the entire slab without the +U correction.
Figure A.5: Comparison of different levels of theory. (a) Adsorption energies of bent CO$_2$ on stoichiometric and reduced surface sites. (b) Spin densities of O$_{v}$/TiO$_2$ at two different levels of theory, one with the +U correction (U = 2.5 eV) and one without the correction.
A.6 Gas-Phase CO\(_2\) Density of States

Figure A.6: The projected density of states (DOS) comparing CO\(_2\) desorbed (∼5.5 Å above the surface) and CO\(_2\) adsorbed on a stoichiometric surface (S1 configuration). The desorbed CO\(_2\) was in a linear form (top), while the adsorbed CO\(_2\) was in a bent form (bottom). The zero eV has been set to the edge of the conduction band. The filled areas indicate occupied states, while unfilled areas represent unoccupied states.

In Figure A.6 we compare the density of states (DOS) of desorbed (linear) CO\(_2\) when it is ∼5.5 Å above the surface, or not interacting with the surface, to the S1 configuration, or TiO\(_2\) adsorbed (bent) to the stoichiometric surface. When CO\(_2\) was not interacting with the surface (essentially the gas phase), it maintained a linear geometry. The CO\(_2\) band had a characteristic peak near -4 eV when free, but the peak spread upon adsorption between -6 eV to -1.5 eV in the valence band region. The spread of the CO\(_2\) band is due to the hybridization between CO\(_2\) and TiO\(_2\). In our previous work we also observed hybridization[12].
## A.7 Summary of Bent CO$_2$ Adsorption

Table A.1: Summary of adsorbed bent CO$_2$ adsorption geometries and calculated charges.

<table>
<thead>
<tr>
<th>Adsorption Site</th>
<th>$E_{ads}$ (eV)</th>
<th>O ($e^-$)</th>
<th>C ($e^-$)</th>
<th>CO$_2$ ($e^-$)</th>
<th>Cu (e)</th>
<th>O-C-O ($^\circ$)</th>
<th>O-C (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>-0.20</td>
<td>-0.48, -0.66</td>
<td>+0.86</td>
<td>-0.28</td>
<td>NA</td>
<td>131.3</td>
<td>1.20, 1.33</td>
</tr>
<tr>
<td>S2</td>
<td>-0.28</td>
<td>-0.54, -0.60</td>
<td>+0.79</td>
<td>-0.35</td>
<td>+0.54</td>
<td>135.6</td>
<td>1.25, 1.27</td>
</tr>
<tr>
<td>R1</td>
<td>-1.28</td>
<td>-0.38, -0.37</td>
<td>+0.02</td>
<td>-0.74</td>
<td>NA</td>
<td>134.8</td>
<td>1.25, 1.27</td>
</tr>
<tr>
<td>R2</td>
<td>-0.85</td>
<td>-0.35, -0.56</td>
<td>+0.35</td>
<td>-0.56</td>
<td>+0.02</td>
<td>127.2</td>
<td>1.22, 1.32</td>
</tr>
<tr>
<td>R3</td>
<td>-1.30</td>
<td>-0.35, -0.57</td>
<td>+0.28</td>
<td>-0.63</td>
<td>+0.06</td>
<td>125.4</td>
<td>1.22, 1.33</td>
</tr>
<tr>
<td>R4</td>
<td>-1.29</td>
<td>-0.38, -0.37</td>
<td>+0.01</td>
<td>-0.74</td>
<td>+0.50</td>
<td>133.7</td>
<td>1.24, 1.27</td>
</tr>
</tbody>
</table>

NA = Not Applicable

In Table A.1, we show data for the bent CO$_2$ geometries discussed in the main text and calculated atomic DDEC6 [113, 114] charges. The O-C-O angles of the bent CO$_2$ are given, as well as the C-O bond distances of CO$_2$. Also listed are the individual atomic DDEC6 charges of the CO$_2$ and Cu metal atoms after the adsorption process.
A.8 CO$_2$ Dissociation Geometries

Figure A.7: Final geometries after CO$_2$ dissociation to CO and O. Shown is CO$_2$ dissociated over several surfaces: a stoichiometric surface (S1), a stoichiometric surface with a Cu adatom (S2), a reduced surface with an oxygen vacancy (R1), a reduced surface with a Cu adatom in an oxygen vacancy (R2), a surface with Cu near an oxygen vacancy (R3), and a surface with Cu far from the oxygen vacancy (R4). The CO$_2$ dissociation energies are indicated.

In Figure A.7 we show the optimized geometries after CO$_2$ had dissociation at each adsorption site. For each dissociation geometry, we tried three different initial configurations at each site to determine the most stable dissociation geometry: adsorbed O and the O atom of CO filling the O$_v$, C filling the O$_v$ and O adsorbed nearby, and adsorbed CO with the dissociated O filling the O$_v$. CO$_2$ dissociation with the dissociated O atom filling the vacancy was the most stable configuration for all CO$_2$ dissociation geometries.
A.9 Transition State Calculations

Figure A.8: The calculated climbing image nudged elastic band (CINEB) pathways for CO$_2$ dissociation. (a) Cu over a stoichiometric surface (S2), (b) TiO$_2$ with an O$_v$ (R1), (c) Cu over a stoichiometric surface (S2) with a photoexcited electron (+ e$^-$), (d) TiO$_2$ with an O$_v$ (R1) + e$^-$, (e) Cu in an O$_v$ (R2) + e$^-$, (f) Cu near an O$_v$ (R3) + e$^-$, (g) Pt over a stoichiometric surface (S2), (h) Pt in an O$_v$ (R2), and (i) Pt near an O$_v$ (R3). The reaction barriers are shown in the upper right corner of each pathway in eV.

Figure A.8 shows the other calculated CO$_2$ dissociation pathways that were not given in the main text. In Figure A.8a, there were two energy valleys, one between image 3 and 5 and the other between 9 and 11. Essentially the CO$_2$ molecule has to rotate to interact with the Cu atom before it can dissociate. In Figure A.8b,
the activation barrier was 0.95 eV for R1 configuration, which had CO₂ in an O₂. This activation energy was comparable to the values reported by Sorescu et al.[34] (0.90 eV) and Ji and Luo[88] (0.73 eV). In Figures SA.8c-f, the CINEBs show the dissociation pathways and barriers taking a photoexcited electron into account. All of the minimum energy pathways with the photoexcited electron models have similar pathways to their counterparts with no photoexcited electron. For example, in Figure A.8c, there were two energy valleys, similar to Figure A.8a. In Figure A.8g, there was an energy valley between images 7 and 8 for the Pt/TiO₂ (S2) case. This valley is a metastable state that the CO₂ must reach in order to dissociate. There are two peaks between the initial and final state of the dissociation pathway, and for the reaction barrier we used the highest peak between the initial and final images. In Figures SA.8h and i, the CO₂ activation barrier was found to be 0.43 eV and 0.46 eV, respectively. Given the these two pathways have similar initial and final states in the nudge elastic band calculations, the similar activation energies are not surprising.
A.10 Photoexcited Electron Model

Figure A.9: CO$_2$ adsorption in the presence of a "photoexcited" electron, similar to the work of He et al.[5] A hydrogen atom, which provides an electron upon adsorption, was added to the surface a distance away from the CO$_2$ adsorption site.

Figure A.9 shows the photoexcited electron model, similar to the work by He et al.[5], which has an extra electron in the surface due to the presence of a hydrogen atom. We placed the electron donor, a hydrogen adatom, far from the O$_x$ to prevent any possible hydrogen interactions with the CO$_2$ or reduced Ti atoms. Table A.2 shows the calculated atomic charges on Cu in the presence of an unpaired electron. We note that the charge on the H adatom did not change when Cu adsorbed to the surface. However, for some cases the Cu atom charges were slightly more positive.
when no unpaired electron was present compared to when an unpaired electron was present, being 0.11 e\(^{-}\) for Cu in an O\(_v\), and 0.08 e\(^{-}\) for Cu near an O\(_v\). Such a small shift could be due to computational noise of the DFT method or the DDEC6 method of charge analysis. We did not see any significant change of charges for any other atoms.

Table A.2: Calculated atomic charges for adsorbed Cu with an unpaired electron and without an unpaired electron.

<table>
<thead>
<tr>
<th>Adsorption Site</th>
<th>(E_{ads}) (eV)</th>
<th>Cu (e)</th>
<th>H (e)</th>
<th>(E_{ads}) (eV)</th>
<th>Cu (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/TiO(_2)</td>
<td>-2.21</td>
<td>+0.50</td>
<td>+0.45</td>
<td></td>
<td>-2.30</td>
</tr>
<tr>
<td>Cu in O(_v)</td>
<td>-2.66</td>
<td>-0.24</td>
<td>+0.45</td>
<td>-2.23</td>
<td>-0.35</td>
</tr>
<tr>
<td>Cu near O(_v)</td>
<td>-2.56</td>
<td>-0.24</td>
<td>+0.45</td>
<td>-2.12</td>
<td>-0.32</td>
</tr>
<tr>
<td>Cu far O(_v)</td>
<td>-2.28</td>
<td>+0.50</td>
<td>+0.45</td>
<td>-2.26</td>
<td>+0.50</td>
</tr>
</tbody>
</table>
Table A.3 shows the bent CO$_2$ adsorption energies and charges when an unpaired electron was present. CO$_2$ bound 0.05 eV to 0.28 eV more strongly to the surface when an unpaired electron was present. Also notice that all Cu charges were positively charged after bent CO$_2$ adsorption.
Figure A.10: Adsorption energies of linear and bent CO$_2$ over various surfaces with the presence of an photoexcited electron.

In Figure A.10 we show the adsorption energies of linear and bent CO$_2$ across the six sites with the presence of an photoexcited electron. The trend stayed the same as the regular model (with no extra electron) that over the reduced surfaces bent CO$_2$ is preferred over linear CO$_2$; over the stoichiometric surface linear CO$_2$ is more stable than bent CO$_2$. The highest selectivity of bent CO$_2$ in the presence of an photoexcited electron still still occurs when Cu is near O$_v$ (R3).
A.11 Pt Adsorption and Bent CO$_2$ over Pt/O$_v$

Figure A.11: Bent CO$_2$ adsorption geometries over TiO$_2$ and Pt/TiO$_2$ surfaces. Shown is CO$_2$ adsorption over several surfaces: a stoichiometric surface (S1), a stoichiometric surface with a Pt adatom (S2), a reduced surface with oxygen vacancy (R1), a reduced surface with a Pt adatom in an oxygen vacancy (R2), a surface with Pt near an oxygen vacancy (R3), and a surface with Pt far from the oxygen vacancy (R4). The CO$_2$ adsorption energies are indicated.

Figure A.11 shows the bent CO$_2$ adsorption geometries and energies at the six Pt sites, similar to Figure 5 in the main text. R2 and R3 had similar optimized geometries which were discussed in the main text. Table A.4 shows the calculated charges of adsorbed Pt atoms compared with adsorbed Cu atom. Notice that Pt stayed negatively charged in all four configurations, whereas Cu over stoichiometric TiO$_2$ and far from the O$_v$ are positively charged.
Table A.4: Calculated adsorption energies and charges of Pt and Cu over TiO$_2$ surfaces.

<table>
<thead>
<tr>
<th>Adsorption Site</th>
<th>$E_{ads}$ (eV)</th>
<th>Pt (e)</th>
<th>Cu (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>-2.30</td>
<td>+0.50</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>-2.23</td>
<td>-0.35</td>
<td></td>
</tr>
<tr>
<td>M/TiO$_2$</td>
<td>-3.31</td>
<td>-0.23</td>
<td></td>
</tr>
<tr>
<td>M in O$_v$</td>
<td>-5.37</td>
<td>-0.70</td>
<td></td>
</tr>
<tr>
<td>M near O$_v$</td>
<td>-5.37</td>
<td>-0.70</td>
<td></td>
</tr>
<tr>
<td>M far O$_v$</td>
<td>-3.14</td>
<td>-0.23</td>
<td></td>
</tr>
</tbody>
</table>

Table A.5: Bent CO$_2$ atomic charges and CO$_2$ geometry information over Pt/TiO$_2$.

<table>
<thead>
<tr>
<th>Adsorption Site</th>
<th>$E_{ads}$ (eV)</th>
<th>O (e)</th>
<th>C (e)</th>
<th>CO$_2$ (e)</th>
<th>Pt (e)</th>
<th>O-C-O ($^\circ$)</th>
<th>O-C (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>-0.20</td>
<td>-0.48</td>
<td>-0.66</td>
<td>+0.86</td>
<td>-0.28</td>
<td>NA</td>
<td>131.3</td>
</tr>
<tr>
<td>S2</td>
<td>-0.05</td>
<td>-0.54</td>
<td>-0.56</td>
<td>+0.80</td>
<td>-0.30</td>
<td>-0.15</td>
<td>130.3</td>
</tr>
<tr>
<td>R1</td>
<td>-1.28</td>
<td>-0.38</td>
<td>-0.37</td>
<td>+0.02</td>
<td>-0.73</td>
<td>NA</td>
<td>134.8</td>
</tr>
<tr>
<td>R2</td>
<td>-0.71</td>
<td>-0.38</td>
<td>-0.58</td>
<td>+0.45</td>
<td>-0.51</td>
<td>-0.45</td>
<td>125.1</td>
</tr>
<tr>
<td>R3</td>
<td>-0.64</td>
<td>-0.38</td>
<td>-0.58</td>
<td>+0.48</td>
<td>-0.48</td>
<td>-0.51</td>
<td>126.0</td>
</tr>
<tr>
<td>R4</td>
<td>-1.47</td>
<td>-0.38</td>
<td>-0.38</td>
<td>+0.02</td>
<td>-0.74</td>
<td>-0.22</td>
<td>134.0</td>
</tr>
</tbody>
</table>

NA = Not Applicable

In Table A.5, we show data on bent CO$_2$ adsorption geometries and calculated atomic DDEC6 charges over the Pt/TiO$_2$ surfaces. The O-C-O angles of the bent CO$_2$ are given as well as C-O distances. Atomic DDEC6 charges are also given. Notice that all Pt atoms were negatively charged after bent CO$_2$ adsorption, which is different from the Cu case as seen in Table A.1.
Appendix B

Experimental Results

This experimental work was performed by Thomas Fenton and Professor Gonghu Li from the Department of Chemistry in University of New Hampshire, and Alexander Carl and Professor Ronald Grimm from the Department of Chemistry in WPI. We kindly acknowledge and thank their experimental contribution. The experimental methodology can be found in Appendix B.1, and the experimental results can be found in Appendix B.2 and B.3.

B.1 Experimental Methodology

P25 TiO$_2$ was obtained from Evonik and used as received. Cu/TiO$_2$ was synthesized via surface adsorption. In a typical synthesis, 500 mg of dried TiO$_2$ was dispersed in 75 mL Milli-Q and sonicated for 10 minutes. 100 mg of CuCl$_2$ (Sigma-Aldrich, 99.995%) was then added to the TiO$_2$ suspension under constant stirring. The resulting mixture was stirred at room temperature for 12 hours before Cu/TiO$_2$ was recovered via centrifugation and was washed with Milli-Q water for three times. The Cu/TiO$_2$ sample was then dried at 90° C for 2 hours.

Thermal treatment of powder samples was conducted in a Harrick Praying Man-
tis diffuse reflectance accessory in a Thermo Nicolet 6700 FTIR spectrometer. A small amount of TiO$_2$ or Cu/TiO$_2$ was placed in the sample holder of the accessory, purged with Ar at room temperature, and then annealed at 300$^\circ$ C for 1 hour under 5% H$_2$ (95% Ar) or O$_2$ prior to further CO$_2$ adsorption and photochemical studies.

The synthesized Cu/TiO$_2$ sample was examined using transmission electron microscopy (TEM, Zeiss/LEO 922 Omega). The loading of Cu on TiO$_2$ was quantified using a Varian Vista AX induced coupled plasma atomic emission spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI5600 system[129]. UV-visible spectra of powder samples were obtained on a Cary 50 Bio spectrophotometer. A Barrelino diffuse reflectance probe was used to collect UV-visible spectra of powder samples using BaSO$_4$ as a standard. For studies with XPS and UV-visible spectroscopy, thermal treatment was carried out in a STF 1200 tube furnace at 300$^\circ$ C under 5% H$_2$ (95% Ar) or O$_2$.

**B.2 Experimental Results on CO$_2$ Activation and O$_x$**

Highly dispersed Cu sites on TiO$_2$ were prepared via a simple adsorption method, in which Cu$^{2+}$ cations were adsorbed onto TiO$_2$ nanoparticles suspended in an aqueous solution of CuCl$_2$. The synthesized sample was thermally treated under H$_2$ (to produce oxygen vacancies) or under O$_2$. See the Methodology for further details. Quantification with elemental analysis indicated a loading of 20.5 $\mu$mol Cu per gram TiO$_2$, corresponding to a coverage of 1 Cu atom per 5 nm$^2$ surface area on TiO$_2$[29]. Examination with microscopy confirmed the absence of Cu aggregates or nanoparticles in the synthesized Cu/TiO$_2$ material (Figure B.3). Thermal treatment with H$_2$ resulted in the formation of oxygen vacancies in Cu/TiO$_2$, as shown by
Figure B.1: FTIR spectra of species formed upon CO$_2$ adsorption on (a) H$_2$-treated TiO$_2$, (b) H$_2$-treated Cu/TiO$_2$, and (c) O$_2$-treated Cu/TiO$_2$ in the spectral region between 1500 cm$^{-1}$ and 1800 cm$^{-1}$. The spectra are fitted to individual bands with Lorentzian line-shapes. The fitted peak at 1638 cm$^{-1}$, corresponding to bent CO$_2$, is indicated by distinct coloring for each sample.

The peak at 1638 cm$^{-1}$ is also present, with greater intensity, in the spectrum of H$_2$-treated Cu/TiO$_2$ (Figure B.1b). In comparison, this peak is much less intense in the spectrum of O$_2$-treated Cu/TiO$_2$ (Figure B.1c). The presence of bent CO$_2$ molecules on O$_2$-treated Cu/TiO$_2$ is likely due to the fact that surface Cu sites stabi-
lize the formation of bent CO\textsubscript{2}, as indicated in our prior work\cite{29} and current work. We conclude therefore based these experimental spectra and peak intensities that bent CO\textsubscript{2} forms with the following intensities: Cu/O\textsubscript{v}TiO\textsubscript{2} > O\textsubscript{v}TiO\textsubscript{2} > Cu/TiO\textsubscript{2} > TiO\textsubscript{2}. This is in agreement with our DFT calculations.

In our photochemical studies, thermally treated TiO\textsubscript{2} or Cu/TiO\textsubscript{2} was subject to irradiation with UV light in the presence of gaseous CO\textsubscript{2}. Difference FTIR spectra were obtained by subtracting infrared spectra after light irradiation from corresponding spectra before light irradiation. A peak at 2111 cm\textsuperscript{-1} is clearly seen in the difference spectrum of H\textsubscript{2}-treated Cu/TiO\textsubscript{2}, indicating the formation of CO adsorbed on Cu\textsuperscript{+} sites upon light irradiation (Figure B.2b). This peak is also observed in the spectrum of O\textsubscript{2}-treated Cu/TiO\textsubscript{2} but with much lower intensity (Figure B.2c). Since a much greater amount of bent CO\textsubscript{2} molecules were produced by H\textsubscript{2}-treated Cu/TiO\textsubscript{2} than O\textsubscript{2}-treated Cu/TiO\textsubscript{2} (Figure B.1), the comparison between the spectra shown in Figure B.2b and B.2c suggests that the increased number of bent CO\textsubscript{2} molecules promoted photoinduced dissociation of CO\textsubscript{2} on the TiO\textsubscript{2} materials. CO\textsubscript{2} dissociation may also have been facilitated by lower barriers, as our calculations show, over H\textsubscript{2}-treated Cu/TiO\textsubscript{2} which would presumably have more O\textsubscript{v}. Formation of CO by photoinduced dissociation of CO\textsubscript{2} likely occurred on H\textsubscript{2}-treated TiO\textsubscript{2} as well, but was not observed in the spectrum shown in Figure B.2a due to the absence of surface sites (such as Cu\textsuperscript{+}) for strong CO adsorption. These results, again in agreement with our DFT results, indicate that O\textsubscript{v} and Cu may increase CO\textsubscript{2} reduction activity.
Figure B.2: Difference FTIR spectra of (a) H$_2$-treated TiO$_2$, (b) H$_2$-treated Cu/TiO$_2$, and (c) O$_2$-treated Cu/TiO$_2$ after photochemical CO$_2$ reduction for 1 h.

**B.3 Experimental Characterization**

Further details on our experimental results are given. Figure B.3 provides transmission electron microscopy (TEM) images of our Cu/TiO$_2$ samples. Figure B.4 provides UV-visibility spectra of various samples. Figure B.5 provides x-ray photoelectron spectra of various samples. Figure B.6 provides FTIR spectra of untreated TiO$_2$ after CO$_2$ adsorption.
Figure B.3: TEM images of Cu/TiO$_2$ at different magnifications: (a) scale bar 50 nm, (b) scale bar 10 nm.
Figure B.4: UV-visible spectra of (a) untreated Cu/TiO$_2$, (b) H$_2$-treated Cu/TiO$_2$, and (c) O$_2$-treated Cu/TiO$_2$.

Figure B.5: Cu 2p XPS spectra of (a) untreated Cu/TiO$_2$, (b) H$_2$-treated Cu/TiO$_2$, and (c) O$_2$-treated Cu/TiO$_2$. Peaks associated with Cu$^{2+}$ (934.5 eV) and Cu$^+$ (932.2 eV) are seen in (a), but only the Cu$^+$ peak is seen in (b) and (c).
Figure B.6: FTIR spectrum of species formed upon CO$_2$ adsorption on untreated TiO$_2$. 