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Imaging Catalytic Activation of CO₂ on Cu₂O (110): A First-Principles Study

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Abstract

Balancing global energy needs against increasing greenhouse gas emissions requires new methods for efficient CO₂ reduction. While photoreduction of CO₂ is promising, the rational design of photocatalysts hinges on precise characterization of the surface catalytic reactions. Cu₂O is a promising next-generation photocatalyst, but the atomic-scale description of the interaction between CO₂ and the Cu₂O surface is largely unknown, and detailed experimental measures are lacking. In this study, density-functional theory (DFT) calculations have been performed to identify the Cu₂O (110) surface stoichiometry that favors CO₂ reduction. To facilitate interpretation of scanning tunneling microscopy (STM) and X-ray absorption near-edge structures (XANES) measurements, which are useful for characterizing catalytic reactions, we present simulations based on DFT-derived surface morphologies with various adsorbate types. STM and XANES simulations were performed using the Tersoff-Hamann approximation and Bethe-Salpeter equation (BSE) approach, respectively. The results provide guidance for observation of CO₂ reduction reaction on, and rational surface engineering of, Cu₂O (110). They also demonstrate the effectiveness of computational image and spectroscopy modeling as a predictive tool for surface catalysis characterization.

Graphical Abstract

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Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xx.xxxx/acs.chemma-ter.xxxxxxx. Molecular adsorption energies by various dispersion correction schemes (Section S1), O₂ energy correction (Section S2), Relationship between Cu Bader charges and formal oxidation states (Section S3), Simulated STM images of CO and CO₂ on defected Cu₂O(110) surface (Section S4), and Simulated Cu K-edge XANES of top-four-layer Cu atoms on ideal surface (Section S5) (PDF)

1. INTRODUCTION

Photoreduction of gaseous CO_2 to solar fuels has attracted considerable attention over the past few decades as a technically viable and environmentally responsible means to mitigate global warming and energy crises.^{1–3} Reduction of CO_2 is an energetically demanding process that involves multiple proton-coupled electron transfer reactions,^{4–9} so a properly functioning photocatalyst is critical. For catalyzing CO_2 reduction, the feasibility of using a wide variety of semiconductor materials, including ZnO ,^{10,11} $\alpha\text{-Fe}_2\text{O}_3$,^{12,13} GaAs ,^{14,15} and TiO_2 ,^{16–21} has been explored extensively both experimentally and theoretically. Of these, TiO_2 has been suggested to be the most suitable photocatalyst for driving solar fuel production, due to its abundance and outstanding chemical stability.²² However, the wide band gap of TiO_2 (3.0 eV to 3.2 eV) limits its sunlight absorption to the ultra-violet region, resulting in limited energy conversion efficiency. Therefore, the search for next-generation efficient photocatalyst is of foremost importance.

Cu_2O has been identified as a particularly attractive candidate to facilitate CO_2 photoreduction due to its unique electronic, optical, and chemical properties.^{23–27} It has a direct band gap of 2.17 eV,²⁸ low electron affinity, and high optical absorption of the solar spectrum. It has been shown theoretically that photocatalytic reduction of CO_2 to methanol is thermodynamically feasible on Cu_2O surfaces.²⁹ The practical use of Cu_2O as an electrocatalyst for CO_2 reduction, however, is relatively challenging because of the poor stability of Cu_2O in aqueous solution at reducing electrochemical potentials. Nonetheless, it was demonstrated that hybrid $\text{CuO-Cu}_2\text{O}$ nanorod arrays maintain reasonable stability during photoelectrochemical reduction of CO_2 to methanol.^{30,31} Recent experimental work has also found enhanced CO_2 photoreduction using heterostructures formed by Cu_2O and either TiO_2 ³² or Fe_2O_3 ,³³ but detailed understanding of the interaction between CO_2 and Cu_2O as a photocatalyst is still limited.

Different surface facets of catalysts often show different stabilities and activities. For Cu_2O , nanocrystals with specific morphologies can be obtained by shape-controlled synthesis routines using hydrazine as the reducing agent.³⁴ Cu_2O nanocrystals with (100) and (110) surfaces gradually decompose to nanosheets during photocatalytic reactions, while (111) surface shows the highest stability,³⁵ which is in excellent agreement with theoretical predictions of orientation-dependent surface stability.²⁹ In addition, while Cu_2O octahedra with exposed (111) surfaces possess much higher activity than cubes with exposed (100)

facets,³⁴ rhombic dodecahedral nanocrystals that only expose (110) facets show optimal catalytic performance.³⁶ Therefore, for Cu₂O, while the (111) surface possesses the highest stability among all three low-index surfaces, the (110) surface likely yields superior photocatalytic activity.

Thus far, however, the vast majority of experimental and theoretical efforts have been devoted to understanding the catalytic behaviors of Cu₂O (111) surface.^{37–42} For instance, an X-ray photoemission spectroscopy (XPS) investigation has been performed to study the adsorption of CO₂ on Cu₂O (111),⁴³ and the effect of surface defects on the interaction between H₂O and the Cu₂O (111) surface has been studied using scanning tunneling microscopy (STM).⁴¹ Corresponding density-functional-theory (DFT) work has also been carried out systematically to investigate the adsorption of CO₂ (Ref. 40) and H₂O (Ref. 42) molecules on both ideal and defected Cu₂O (111) surfaces. In contrast, the photocatalysis-related properties of the (110) surface have received much less attention,⁴⁴ and the interaction mechanism of CO₂ with (110) surface remains elusive. Therefore, in the current study, we focus on the interaction of CO₂ with the Cu₂O (110) surface.

As mentioned before, the complete conversion of CO₂ to solar fuels is a multi-step process involving several intermediate products. The initial, “activation” step of the reaction, during which CO₂ draws electrons from the catalyst and adsorbs on the surface, is often the rate-limiting step due to the inertness of CO₂ molecules.^{45–47} After activation, CO is obtained by transferring two electrons to the CO₂, and for several catalysts, such as the rutile TiO₂⁴⁸ and CuGaO₂ particles,⁴⁹ CO is the primary product while the generation of hydrocarbons is quite limited. Hence, it is also important to investigate the interaction of CO with the catalyst surfaces to obtain a comprehensive understanding of the reaction path. Furthermore, the surface catalytic performance under various operational conditions are largely affected by surface inhomogeneities.^{40,48} We therefore investigate the interactions of both CO₂ and CO on pristine and defected Cu (110) surfaces.

Many experimental techniques that probe surface and bulk properties have been utilized in photocatalysis research. STM experiments, which are sensitive to atomic-scale structure and electronic properties of the surfaces and molecular adsorbates, have been successfully carried out to monitor the adsorption and dissociation of CO₂ on rutile TiO₂(110),⁵⁰ and STM images have been simulated based on models of surface defects and adsorbed H₂O on the same surface.⁵¹ Önste *et al.* utilized STM to study the atomic structure of Cu₂O (111).³⁹ They proposed two tentative structural models for the unreconstructed surface and ($\sqrt{3} \times \sqrt{3}$) reconstruction, but no STM images simulation has been performed using corresponding models to determine the exact structure observed experimentally. X-ray absorption near-edge structure (XANES), which is sensitive to the oxidation states and local chemical environments, has also been an effective tool to characterize Cu-based systems.^{52–54} The creation of surface defects and the activation of CO₂ both alter the charge state of surface atoms. XANES spectra is capable of indicating surface stoichiometry and local chemistry change induced either by intrinsic defects or extrinsic adsorbates.

Experimentally, it is difficult to recognize all intermediate products due to insufficient temporal and spatial resolutions of measurements. Moreover, even if an intermediate product

is probed in the experimental imaging during the reduction reaction, the exact species and configuration of this product often cannot be accurately determined. Multi-modal measurements, together with the accurate simulation of experimental signals using atomistic models derived from DFT calculations, can identify the intermediate species and reaction pathway. In this study, we first perform DFT calculations to investigate the adsorption of CO₂ and CO on ideal and defected Cu₂O (110) surfaces and determine the preferable surface chemistry for CO₂ activation. STM image and XANES simulations are subsequently carried out based on the DFT surface structures with various adsorbate configurations. We demonstrate that the computational image and spectroscopy simulations can directly map the experimental observations to the underlying surface chemistry, and therefore effectively interpret experimental measurements and assist in rational catalyst design.

2. COMPUTATIONAL METHODS

The Vienna Ab-initio Simulation Package (VASP)^{55,56} was used to perform DFT calculations to simulate the Cu₂O (110) surface geometries and the energetics of CO₂/CO adsorption. Projector-augmented wave (PAW)⁵⁷ atomic pseudopotentials were used in conjunction with a cutoff energy of 400 eV for the plane-wave basis set. The generalized-gradient approximation (GGA) with the parametrization of Perdew-Burke-Ernzerhof (PBE) was used for the exchange-correlation functional.⁵⁸ GGA gives poor description of the correlation effects of 3*d* electrons, so that the formation energies 3*d* transition metal oxides are generally in error. For instance, the reaction enthalpy of the reaction $Cu_2O + \frac{1}{2}O_2 = 2CuO$ calculated using PBE functional is -1.84 eV, while the experimental value is -1.47 eV.⁵⁹ On-site Coulomb interaction between the localized 3*d* electrons was accounted for using the DFT+*U* approach proposed by Dudarev,⁶⁰ with a *U*-*J* value of 4 eV applied on Cu, as calibrated by Wang *et al.* to correct the calculated reaction enthalpy of the abovementioned reaction.⁶¹ The semilocal character of GGA functionals results in poorly-described long-range dispersion interactions, which is expected to be nontrivial for Cu₂O surface with adsorbed molecular species. The DFT-D2 method of Grimme⁶² was employed previously to study the adsorption of CO₂ on Cu₂O (111) surfaces.⁴⁰ However, there are other corrections, e.g. DFT-D3,⁶³ as well as van der Waals (vdW)-inclusive functionals^{64–67} available for dispersion interactions. We compared the molecular adsorption energies obtained using PBE+*U*, PBE+*U*-D2, PBE+*U*-D3 and other vdW-inclusive functionals in Section S1 of the supporting information (SI). It was found that the molecular adsorption energies obtained using PBE+*U* are in general higher than those using other functionals, and the adsorption energies obtained using PBE+*U*-D2⁶² and optB86b-vdW⁶⁴ are very close to each other. The adsorption energies reported in this work used PBE+*U*-D2 for better comparison with previous theoretical work.⁴⁰ In addition, the reaction enthalpy of $Cu_2O + \frac{1}{2}O_2 = 2CuO$ obtained using PBE+*U*-D2 is -1.41 eV, in close agreement with the experimental value of -1.47 eV.⁵⁹ The calculated Cu₂O lattice parameter is 4.30 Å, which is in close agreement with the experimental value of 4.27 Å.⁶⁸ The Kohn-Sham gap of bulk Cu₂O is found to be 0.64 eV, in comparison with the experimental value of 2.17 eV.²⁸

The Cu₂O (110) surface was modeled using a (2×4) surface slab with 2 repetition units along the [001] direction and 4 repetition units along the [1 $\bar{1}$ 0] direction, respectively, as

shown in Fig. 1a. The slab consisted of 7 alternating Cu-O and Cu layers and the bottom layer was kept fixed during the relaxation. A vacuum spacing of approximately 17 Å along the [110] direction separates each slab from its periodic images to prevent unphysical coupling. CO₂ and CO molecules were adsorbed onto one side of the slab and a dipole correction⁶⁹ was applied. The positions of all atoms, except the bottom layer, were allowed to relax in all three directions until the force components acting on each atom were less than 0.01 eV/Å. All calculations were spin-polarized. The Brillouin-zone was sampled using a 3×2×1 Monkhorst-Pack grid.⁷⁰ Electron smearing was carried out near the Fermi surface using Gaussian smearing with a width of 0.05 eV. Convergence tests were performed by varying the computational parameters such as slab thickness, planewave cutoff energy, Brillouin-zone sampling grid and vacuum size, and the variations in the adsorption energies were found to be within 10 meV.

Calculations for O₂, CO and CO₂ molecules were performed using a 15 Å×16 Å×17 Å cell. The O₂ energy obtained by PBE-D2 was corrected following the procedure described by Wang *et al.*⁶¹ and Grindy *et al.*⁷¹, and a 0.274 eV correction was added to the DFT calculated energy of O₂ molecule. Details are shown in Section S2 in the SI. The adsorption energy of atomic/molecular species on the surface slab is defined as

$$E_{ads} = E_{atom/mol + sub}^{tot} - (E_{sub} + E_{atom/mol}) \quad (1)$$

where $E_{atom/mol + sub}^{tot}$ is the total energy of the system after an O atom, or CO/CO₂ molecule is adsorbed on the substrate, E_{sub} is the energy of the substrate before adsorption, and $E_{atom/mol}$ is half of the corrected O₂ energy or the energy of an isolated CO or CO₂ molecule. Zero-point energies were not included in the adsorption energy calculations.

To infer the oxidation state of Cu atoms, the Bader charges⁷² of Cu atoms in bulk Cu, Cu₂O, Cu₄O₃ and CuO were calculated and fitted with a linear least-squares fit to the formal oxidation states of Cu (0 in Cu, +1 in Cu₂O, both +1 and +2 in Cu₄O₃, and +2 in CuO). The Bader charge values of Cu atoms in the surface slabs can accordingly be mapped to Cu oxidation states using the fitting result. Detailed information is presented in Section S3 in the SI. The reaction barrier of CO₂ dissociation on the surface is calculated using climbing-image nudged elastic bands (CI-NEB) method.⁷³ STM images were calculated within the Tersoff-Hamann approximation,⁷⁴ in which the constant-current STM image is modeled as a surface of constant charge density from Kohn-Sham eigenstates corresponding to eigenenergies within a certain range.

The XANES signal of various Cu₂O (110) surface structures were simulated using the OCEAN package^{75,76} that implements the Bethe-Salpeter equation (BSE), which is built upon a DFT ground-state calculation. The ground-state charge density, and the wavefunctions used in core-hole screening and BSE calculations, were obtained using the Quantum Espresso⁷⁷ package. The Local-Density Approximation (LDA) was used as the exchange-correlation functional. Norm-conserving pseudopotentials from the ABINIT⁷⁸ distribution were used, in conjunction with a cutoff energy of 952 eV. In particular, the core

and valence configurations of Cu pseudopotential are $[\text{Ar}]3d^{10}4s^1$. To test the validity of the pseudopotentials, the bulk Cu_2O Cu K-edge was also computed using a 2850 eV cutoff energy together with a neon-core Cu pseudopotential with the configuration of $[\text{Ne}]3s^23p^63d^94s^0$, which was generated using the OPIUM⁷⁹ package. Essentially no qualitative difference was found in the simulated Cu_2O Cu K edge obtained by the two different pseudopotentials, in terms of the peak positions and relative intensity. The comparison of spectra is shown in Fig. 9.

The surface configurations obtained from DFT calculations were used for XANES simulations. Both Kohn-Sham states and core-hole screening calculations used a $3\times 2\times 2$ k-point grid for Brillouin-zone sampling. All surface calculations included 1700 bands. Three photon polarization directions, $[001]$, $[1\bar{1}0]$ and $[110]$, were considered. The final spectrum was obtained by averaging the spectra generated by the Cu atoms in the top three surface layers.

3. RESULTS AND DISCUSSION

3.1. Ideal and Defected Cu_2O (110)

The structural and chemical properties of ideal and defected Cu_2O (110) surfaces without molecular adsorbates were first investigated. The Cu_2O (110) surface structure can be changed by varying the surface termination. In this study, we focus on the surface terminated by both Cu and O atoms as it is observed to be thermodynamically more favorable than Cu-termination under realistic catalytic conditions.^{29,80} The DFT-optimized structures of all surface configurations being considered are shown in Fig. 1. In addition to the defect-free ideal surface (Fig. 1b), O-deficient surface with O vacancies (Fig. 1c) and O-excess surface with additional O atoms are also studied because these are two commonly-observed defect types depending on the treatment procedure and oxygen chemical potential.^{29,81} Two stable adsorption sites for excess O atoms, namely shifted-hollow (ShH) and bridge (B) sites, are identified. As shown in Fig. 1d, the ShH site, or equivalently the on-surface under-coordinated tetrahedral site, is located between two native O atoms along the $[1\bar{1}0]$ direction, whereas the B site is a subsurface adsorption site located between two Cu atoms on the second layer along the $[1\bar{1}0]$ direction (Fig. 1e). The O adsorption energies at ShH and B sites under an oxidizing environment were calculated to be -0.43 eV and -0.40 eV, respectively. The notations of ShH and B were adopted from the work of Duan *et al.*⁸² To examine the likelihood of forming each surface type under different environments, the formation energies of ideal, O-deficient and O-excess surface structures were calculated as a function of oxygen chemical potential,

$$E_{\text{form}} = E_{\text{slab}} - N_{\text{Cu}}\mu_{\text{Cu}} - N_{\text{O}}\mu_{\text{O}} \quad (2)$$

where E_{slab} is the total energy of the surface slab, N_{Cu} and N_{O} are the number of Cu and O atoms in the surface slab, respectively, and μ_{Cu} and μ_{O} are the chemical potentials of Cu and O, respectively, which are correlated through the following equation:

$$2\mu_{Cu} + \mu_O = \mu_{Cu_2O}^{bulk} \quad (3)$$

where $\mu_{Cu_2O}^{bulk}$ is the chemical potential of defect-free bulk Cu₂O that can be approximated by the DFT energy of Cu₂O. The formalism for calculating μ_{Cu} and μ_O under O-rich and O-poor environments was described previously by Bendavid *et al.*²⁹ We define $\Delta\mu_O = \mu_O - \frac{1}{2}E_{O_2}$, where E_{O_2} is the DFT energy of oxygen molecule, so eq. 2 can be rewritten as

$$E_{form} = E_{slab} - N_{Cu}\mu_{Cu} - N_O(\Delta\mu_O + \frac{1}{2}E_{O_2}) \quad (4)$$

Apparently, in the O-rich limit, $\mu_O = 0$ eV. The mixing of PBE and PBE+U energies were taken into account following the procedure of Jain *et al.*⁸³ For the clarity of presentation, Fig. 1f presented the relative formation energy of each surface as a function of μ_O , which is defined as the ratio of the formation energy of a specific surface to the formation energy of ideal surface in the O-rich limit. As shown in Fig. 1f, the ideal surface possesses the lowest formation energy throughout the entire range of oxygen chemical potential. However, at the lower and upper limits of oxygen chemical potential, the formation energies of O-deficient surface and O-excess surfaces are only marginally higher than that of the ideal surface. Therefore, the O-deficient and O-excess surfaces are likely to form under O-poor and O-rich environments, respectively.

Bader analysis on the surface Cu atoms suggests considerable oxidation state change induced by surface defects. The oxidation state of Cu atoms on the top layer of the ideal surface is calculated to be +1.26, whereas on the O-deficient surface, the oxidation state of Cu atoms adjacent to the O vacancy site decreases to +0.57. On the other hand, bringing additional O atoms onto the surface results in over oxidized Cu atoms, as evidenced by the oxidation states of +1.80 and +1.78 for surface Cu atoms adjacent to excess surface O atoms at ShH and B sites, respectively.

As discussed previously, CO₂ activation occurs through the formation of the anion radical CO₂⁻, which requires charge transfer from the catalyst surface to the neutral CO₂ molecule. Bader analysis demonstrates that the surface Cu atoms in the vicinity of O vacancies are more reduced compared with those on the ideal surface, which implies that electrons are more likely to be transferred to CO₂. Therefore, the O-deficient surface is likely the favorable structure for CO₂ activation even without being photoexcited to generate free electrons.

3.2. CO₂ Adsorption on Ideal and Defected Cu₂O (110)

We performed an extensive search on the possible CO₂ adsorption configurations on all four types of surfaces shown in Fig. 1, including parallel, vertical, tilted and bent CO₂ molecules with both monodentate and bidentate binding configurations. Thirty different starting configurations were tested and, with one exception, all configurations led to CO₂ desorption during structural optimization. For the configuration with the CO₂ molecule placed onto the O deficient site, the relaxed adsorption energy was calculated to be -0.09 eV. In the equilibrium adsorption geometry shown in Fig. 2, one of the O atoms in CO₂ resides in the original O vacancy site of the catalyst surface, and the C atom is found to be bound to two surface Cu atoms, resulting in a bent bidentate CO₂ adsorption configuration (denoted as CO_{2,O-vac}). The O-C-O bond angle of the adsorbed CO₂ molecule is 126.1°, and lengths of the two C-O bonds are measured to be 1.20 Å and 1.37 Å (d_{C-O}^1 and d_{C-O}^2 in Fig. 2), respectively. Considering that the calculated C-O bond length of an isolated CO₂ molecule is 1.18 Å, it is clear that CO₂ adsorption is accompanied by bond stretching between the C and directly adsorbed O atom, whereas the length of the other C-O bond varies slightly.

The inset of Fig. 2 shows the charge redistribution between the adsorbed CO₂ molecule and its four neighboring Cu atoms, which was measured by subtracting the charge densities of CO₂ molecule and O-deficient Cu₂O substrate (with the same atomic geometry as the CO₂ adsorbed system) from the charge density of CO₂-containing Cu₂O surface. Clearly, CO₂ adsorption induces electron charge transfer from the surface Cu atoms to the CO₂ molecule, as the charge depletion and accumulation regions are localized around the Cu atoms and the CO₂ molecule, respectively. Bader charge analysis⁷² was also employed to quantify the extent of charge transfer. We compared the surface Cu oxidation states on ideal (Fig. 1a), O-deficient (Fig. 1b) and CO₂-adsorbed (Fig. 2) surfaces, and the results are tabulated in Tab. 1. The surface Cu atoms being sampled in this comparison are labeled in the inset of Fig. 2. As stated above, the oxidation state of Cu1 and Cu2 drops from +1.26 to +0.57 after an O vacancy is created between them. Although Cu3 and Cu4 are relatively far from the vacancy site, their oxidation state also decreases slightly from +1.26 to +1.21. Substantial oxidation state change can be seen when a CO₂ molecule is placed at the O vacancy site: Cu1 and Cu2 have an oxidation state of +1.13 after being bonded to the O atom of the adsorbed CO₂ molecule, which is slightly lower than that of ideal surface Cu, whereas the C atom also draws electrons from Cu3 and Cu4, resulting in oxidation state of +1.42 due to the charge transfer.

Therefore, it is evident that the creation of O vacancies leads to less oxidized surface Cu atoms, and thus provides active sites for CO₂ adsorption by transferring electrons from Cu to the originally inert CO₂. While a defect-free Cu₂O(111) surface supports CO₂ adsorption,⁴⁰ here we show that on the Cu₂O (110) surface, O vacancies are the favored sites to adsorb CO₂ molecules. This O vacancy-facilitated CO₂ adsorption is not unique to the Cu₂O (110) surface. An STM study showed that CO₂ molecules only appear at the O vacancies sites on a rutile TiO₂ (110) surface,⁵⁰ and several surface treatment techniques that have been applied on TiO₂ surfaces to introduce oxygen vacancies,⁸¹ including ion sputtering,⁵⁰ hydrogen thermal treatment⁸⁴ and annealing under oxygen-poor environment,⁸⁵ may also be utilized in Cu₂O surface modification to promote CO₂ activation.

3.3. CO Adsorption on Ideal and Defected Cu₂O (110)

It has been stated that CO can be a prominent intermediate product during CO₂ reduction. On Cu surfaces, however, there is theoretical and experimental evidence suggesting that CO₂ does dissociate upon adsorption.⁸⁶ To evaluate the necessity of including CO in the whole picture of CO₂ reduction on Cu₂O (110), we investigated the plausibility of generating CO by breaking a C-O bond of CO₂ molecule. The CO₂-adsorbed, O-deficient surface shown in Fig. 2 was chosen as the starting configuration, and a CI-NEB calculation was performed to quantify the energy barrier associated with the dissociation process, and the result is shown in Fig. 3. The barrier was calculated to be 0.25 eV. The total energy of the system increases marginally by 0.16 eV after CO₂ dissociation. Therefore, the investigation of CO molecule adsorption on Cu₂O (110) surface is critical, as a CO₂ molecule can easily dissociate into CO and O once CO₂ is adsorbed.

Fig. 4 shows the equilibrium CO adsorption geometries on the ideal and various defected Cu₂O (110) surfaces in Fig. 1. For the adsorption on the ideal surface, all high-symmetry sites on the surface were tested as the initial CO adsorption sites, and three stable adsorption configurations were identified. The CO molecule adsorbed at the top site of surface Cu atom (denoted CuT) results in an adsorption energy of -0.48 eV ($\text{CO}_{\text{ideal}}^{\text{CuT}}$, Fig. 4a). The $\text{CO}_{\text{ideal}}^{\text{H}}$ configuration shown in Fig. 4b is obtained by optimizing an initial structure in which a CO molecule is placed in between two Cu chains along the $[1\bar{1}0]$ direction. The stabilized C atom is bonded to one surface O atom and two surface Cu atoms. It is interesting to note that the $\text{CO}_{\text{ideal}}^{\text{H}}$ structure is essentially the same as the CO₂ adsorbed surface structure shown in Fig. 2, whereas the CO adsorption energy of $\text{CO}_{\text{ideal}}^{\text{H}}$ is -0.63 eV, which is remarkably lower than the CO₂ adsorption energy on the O-deficient surface. The $\text{CO}_{\text{ideal}}^{\text{ShH}}$ configuration shown in Fig. 4c corresponds to the optimized structure in which the CO molecule is adsorbed via a tilt configuration, with the C atom at the ShH site. Unlike the $\text{CO}_{\text{ideal}}^{\text{H}}$ structure, the C atom does not form a bond with the topmost O atoms, but coordinates with a second-layer Cu atom instead. The CO adsorption energy of $\text{CO}_{\text{ideal}}^{\text{ShH}}$ configuration is -0.46 eV, which is comparable to that of $\text{CO}_{\text{ideal}}^{\text{CuT}}$.

We also investigated CO adsorption in the immediate vicinity of the defect sites for the O vacancy and both excess O surfaces. CO adsorption at an O vacancy site (denoted as $\text{CO}_{\text{O-vac}}$ in Fig. 4d) yields a significantly lower adsorption energy of -1.84 eV, with the C atom bonded to three Cu atoms. This relaxed structure is similar to that of $\text{CO}_{\text{ideal}}^{\text{ShH}}$, except that one surface O atom is absent. In fact, the O vacancy site is energetically so competitive for CO adsorption that even if a CO molecule is originally placed at a CuT site or right in between two Cu chains, it ends up embedded at the O vacancy site after structural optimization and results in the $\text{CO}_{\text{O-vac}}$ configuration. Conversely, the binding of CO is significantly less on either excess O surface. In the vicinity of an additional O atom, the CuT site is the only favorable position for CO adsorption. The adsorption energies for surfaces with additional O at the ShH site ($\text{CO}_{\text{O-ShH}}$ as in Fig. 4e) and B site ($\text{CO}_{\text{O-B}}$ as in Fig. 4f) are -0.51 eV and -0.92 eV, respectively. It is worth noting that, because of the elevated

surface O concentration relative to ideal surface, if the CO molecules are initially placed in between two Cu chains as that shown in Fig. 4b), both the on-surface additional O atom and the CO molecule are desorbed from the surface as a CO₂ molecule during structural optimization.

3.4. Electronic Structures of Various Surface Types

To detect the catalytic processes, it is of utmost importance to employ experimental techniques that are able to discriminate between CO₂ and other surface species. STM and XANES can fulfill such a requirement due to their atomic-scale resolution and high sensitivity to local chemical environments, respectively. Nevertheless, having identified the adsorbate configurations on Cu₂O (110) surface from DFT calculations, we note that the experimental observations of these surface adsorbates may be ambiguous and difficult to interpret. Therefore, it is imperative to first assess the experimental signals based on the calculated structural models, so that the experimental measurements can be associated to the underlying surface species. In the following sections, the STM images and XANES of various surface configurations were simulated. Since both STM and XANES probe the local electronic structures, it is instructive to examine the density of states (DOS) of each system. Particularly in STM measurements with an applied bias voltage, the experimental signal is determined largely by the local DOS at the relevant energy level, so examining the theoretical DOS can assist the proper choice of bias voltage in experiments. Fig. 5 shows the total DOS of bulk Cu₂O and the four surface configurations discussed above. In DFT calculations, the Fermi level is placed at the eigenvalue corresponding to the highest occupied Kohn-Sham orbital, i.e., the valence band maximum (VBM). In the ideal and CO-/CO₂-adsorbed surface systems, the surfaces disturb the periodicity of the crystal and lead to surface states, and the defects and adsorbates may also introduce additional energy levels in the band gap. All these effects render the electronic picture of the surface systems complicated. A deep-lying O 2s state is identified at around -19 eV below the VBM in bulk Cu₂O, as indicated in Fig. 5a. In the surface systems shown in Fig. 5b-e, another deep state slightly above the bulk-like O 2s is found (indicated by the arrow in Fig. 5e), which is attributed to the 2s states of surface O atoms that are shifted toward higher energies. The positions of the bulk-like O 2s states relative to the VBM vary within 0.07 eV across the DOS plots listed in Fig. 5. Such a slight deviation of the semi-core O 2s states indicates that the Fermi level shifts caused by defects and adsorbates are negligible.

In STM simulations, the charge density within a certain energy range relative to the Fermi level is evaluated to reflect the bias voltage that is used in experiments. In order to probe the STM signals of both the occupied and unoccupied states of the system, both negative and positive bias voltages were used in our STM simulations. We note that in the simulations, the voltage is relative to the VBM, and in practice Cu₂O is a p-type semiconductor⁸⁷ with Fermi level also close to its VBM, so the negative bias voltages used in the STM simulation corresponds relatively well to the experimentally applied voltages. A negative bias voltage of -2.0 V, corresponding to the charge density roughly in the range of -2.0 eV to 0 eV with respect to the Fermi level, was adopted in the simulations, which was within the experimental bias voltage range in recently reported Cu₂O STM studies.^{39,88} From the insets of Fig. 5b and c, it is clear that the CO_{ideal}^H and CO_{2, O-vac} structures, which are effectively

the same configuration, have a mid-gap state at roughly 0.6 eV above the calculated Fermi level, and the DOS of $\text{CO}_{\text{O-vac}}$ configuration in Fig. 5c shows a peak near the conduction band minimum (CBM). Therefore, a sampling of DOS that roughly covers the energies ranging from the Fermi level and CBM is desirable in order to capture these subtle differences. A positive bias voltage of +1.5 V is therefore selected to sample this region as well as some extended unoccupied region to ensure enough tunneling current. Indeed, as shown in our later discussion, using an excessively high bias voltage (+3.0 V) includes too much DOS far from the Fermi level and result in qualitatively indistinguishable STM topographs of these structures. It is noted that in DFT calculations, the calculated band gap deviates substantially from experimental measurements, so the exact values of the positive voltages used in the simulation do not coincide with realistic experimental conditions, but qualitative trends can still be obtained.

3.5. Simulated STM Images

The simulated STM images of all adsorbate-free surface structures using both negative and positive bias voltages are shown in Fig. 6, and the overlaid structural models indicate the corresponding atom positions. Fig. 6a shows the simulated STM image of the ideal Cu_2O (110) surface, with the bright stripes originating largely from the states of the surface Cu atoms. For the O-deficient surface, the vacancy site appears as a dark depression in the bright stripe when a negative bias voltage is applied, and under positive voltage, the vacancy site is visualized as a bright region, as shown in Fig. 6b. For the O-excess surfaces, O atoms adsorbed at the ShH sites cause additional bright spots under both negative and positive voltages (Fig. 6c). In contrast, the images of surface with an additional O atom at the B sites appear to be strikingly distinct under different voltages (Fig 6d).

Fig. 7 shows the simulated STM topographs of a CO molecule adsorbed on various sites of ideal Cu_2O (110) surface, corresponding to the structures in Fig. 4a–c. In almost all the configurations, the adsorbed molecule appears as a single bright spot, except that of $\text{CO}_{\text{ideal}}^{\text{H}}$ under the positive bias voltage, which exhibits a bright double-lobe shape. The distinct features of simulated STM images validate our choice of bias voltages based on the different electronic structures shown in Fig. 5. Fig. 8 shows the simulated STM topographs of CO or CO_2 molecule adsorbed on defected Cu_2O (110) surfaces. As in Fig. 7, the adsorbed molecules emerge as a nearly circular shape under the negative bias voltage, whereas $\text{CO}_{2,\text{O-vac}}$ configuration results in a double-lobe shape under the positive voltage (Fig. 8b). This feature can be used to identify the adsorption of CO_2 on the O-deficient surface. As shown in Fig. 8c and d, both the images of $\text{CO}_{\text{O-ShH}}$ and $\text{CO}_{\text{O-B}}$ are nearly indistinguishable regardless of bias voltage, which we attribute to the similar bonding environment of the adsorbed CO molecule in these two configurations, as can be seen in Fig 4e and Fig 4f.

The adsorbed CO_2 molecule should be highly distinguishable from CO under STM using a properly applied bias voltage. We note that a relatively small positive bias voltage is essential to capture the CO_2 molecules because the CO_2 adsorption induces a mid-gap state close to Fermi level. Large positive bias voltage includes the unoccupied states far from Fermi level and the effect of mid-gap states thus become less evident. We performed a comparison between the simulated STM images of CO-/ CO_2 -containing systems using

voltages of +1.5 V and +3.0 V, which were in the applied bias voltage range in previous Cu₂O STM studies,⁸⁸ and present the results in Fig. S4 in the SI, from which it can be seen that the STM topographs of these structures under +3.0 V are qualitatively indistinguishable from each other.

In the DFT scheme, the STM signal is approximated using an isosurface of constant partial charge density, with the STM tip being modeled as a dimension-less point. In realistic experiments, however, the shape of the tip is an important factor that affects the image quality, so some of the delicate differences in simulated STM may not be observed. Nevertheless, the CO₂O-vac configuration induces a double-lobe shape that is qualitatively different from the other structures. This feature renders the CO₂ adsorbate distinct from CO. The STM topographs obtained in this study can be used in combination with experiments to identify the surface types, adsorption species and possible reactions.

3.6. Simulated XANES Spectra

Although STM imaging is adequate for capturing the local electronic states, the redox reactions are difficult to identify. We thus calculate the XANES using the DFT structural models to compensate for the lack of oxidation state information from STM. The combination of multi-modal STM and XANES imaging has the advantage of integrating complementary morphofunctional information from different measurements. XANES, especially using grazing incidence⁵⁴ or x-ray nanoprobes,⁸⁹ is increasingly prevalent in the characterization of surface catalytic processes, and in recent years, the simulation of XANES has improved significantly because of improvements in computational techniques. Besides BSE, other methods such as excited-state-core hole (XCH) approach,^{90,91} transition-potential method built upon Gaussian-type-orbital DFT⁹² and atomic-multiplet theory based approaches⁹³ have also been successfully applied in simulating core-level spectra.

The Cu K-edge XANES of various surface configurations were simulated in this study. First, to confirm the validity of the simulation, the K edge of bulk Cu₂O was calculated and compared with experimental spectrum. Fig. 9 demonstrates the remarkable agreement between the simulated and experimental spectra, in which the overall spectrum shape, relative positions and intensities of the peaks were well reproduced. In the experimental spectrum, due to the linear Cu-O-Cu bonds in Cu₂O structure, the first intense peak around 8984 eV is due to the 1s→4p_{x,y} transition, in which *x* and *y* are orthogonal to the Cu-O-Cu bonding direction. The higher energy 1s→4p_z transition is relatively weak and not visible.⁹⁴ The simulated spectra using Cu pseudopotentials with a neon-core ([Ne]3s²3p⁶3d⁹4s⁰) and an argon-core ([Ar]3d¹⁰4s¹) were in close agreement with each other. Considering the substantially lower computational cost, we used an argon-core Cu pseudopotential for the surface calculations.

Focusing on the initial stages of CO₂ catalysis processes, the surface configurations involved in the CO₂ adsorption were calculated. Experimentally, the chemical changes occurring in the specific regions can be selectively resolved owing to the development of high-spatial-resolution X-ray nanoprobes. Grazing-incidence X-ray absorption near edge structure (GIXANES), on the other hand, is also well-suited in surface studies due to the limited

penetration depth and small X-ray incident angles with respect to the surface. Therefore, in the simulation, to capture the reactions taking place on the surface, only the top few layers of the Cu₂O (110) slab were included in the simulation, mimicking the experimental signals collected by X-ray nanoprobe and GIXANES. The spectra computed using the top few layers of Cu atoms on the ideal surface are presented in Fig. S5 in the SI, from which a clearly monotonically correlation between the edge positions and calculated oxidation states of Cu can be observed. Fig. 10 presents the calculated spectra for ideal, O-deficient and CO₂-adsorbed surfaces (CO₂O-vac) using the top three surface layers, and the second derivative of the spectra were also computed. The spectra were aligned by matching the edge positions of the underlying, bulk-like Cu atoms of the surface slabs. In Fig. 10, the three surface configurations yield similar spectra shapes, with subtle changes in the absorption edge energies, which can be inferred from the second derivative. Compared to the ideal surface, the edge position (zero of the second derivative) of the O-deficient surface shifts toward lower energy by roughly 0.3 eV, which is anticipated because the overall oxidation state decreases upon creation of oxygen vacancies on the surface (Tab. 1). After CO₂ adsorption, the edge position shifts slightly back toward higher energy, which corroborates the increase in the surface Cu oxidation states, due to charge transfer to the CO₂ molecule. Therefore, although the spectra appear to be similar, the changes in the surface oxidation states manifest themselves as a shift in the energy of the rising edges. We note that H₂O is also an essential reactant in CO₂ reduction, and the inclusion of H₂O may cause a more pronounced shift of the absorption edge. Further investigation of the interplay between H₂O and CO₂ with larger simulation cells will be the subject of future studies.

The spectra computed by averaging the signals from the top four surface layers (not shown) exhibit the same trend as those obtained from the top three layers, but with smaller shifts in the absorption edge energies, which is due to the smaller fraction of surface atoms being included. It is noted that in the calculations, we utilized simplified surface models with low concentrations of surface defects and adsorbates, which may not sufficiently reproduce the realistic catalytic processes. However, using the model systems and simulated routines as discussed above, the change in the XANES spectra associated with the catalytic processes were adequately captured, and more sophisticated surface configurations and reactions can be predicted by enhancing the modeling system, e.g., by varying the defect and adsorbate concentrations, and including water molecules.

4. CONCLUSIONS

The interactions between CO₂ and ideal and defected Cu₂O (110) surfaces were studied within a first-principles DFT framework and corresponding STM images and XANES were simulated. It was found that the Cu atoms on the oxygen-deficient surface possess extra charge compared with other surface types and are the most active sites for CO₂ adsorption. The adsorption of a CO molecule, an important intermediate product of CO₂ reduction, was also calculated on ideal and defected Cu₂O (110) surfaces. STM topographs were simulated based on all the calculated surface configurations. Due to the mid-gap states induced by adsorbates, it is critical to apply a relatively low positive bias voltage in STM experiments, in order to distinguish the adsorbed CO₂ molecules. XANES spectra of ideal, defected, and CO₂-adsorbed Cu₂O (110) surfaces were also computed within the BSE approximation, and

changes in the spectra due to surface defects and adsorbates are predicted. The computational framework described in this study can readily be utilized to study more intricate catalysis systems and catalytic reactions and to expedite the design of effective catalyst.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) Side (left) and top (right) views of the Cu₂O (110) surface slab model. Blue box indicates the size of the primitive cell of the surface. Relaxed structural models of Cu₂O (110) surface with (b) no surface defects, (c) one O vacancy, and additional O atom at (d) ShH site and (e) B site. Brown, red and blue spheres represent Cu atoms, native O atoms in the oxide and additional O atoms, respectively. (f) Relative formation energies of ideal, O-deficient and O-excess surfaces as a function of oxygen chemical potential. The calculated formation energy of each surface slab is normalized by the formation energy of ideal surface in the O-rich limit ($\mu_{\text{O}} = 0$ eV).

Figure 2. DFT-relaxed geometry of a CO₂ molecule adsorbed at an on-surface oxygen vacancy site. The O-C-O bond angle and C-O bond lengths of the molecule are indicated. The inset shows the charge density difference before and after CO₂ adsorption, with red and green regions indicating charge accumulation and depletion, respectively. Brown spheres represent Cu atoms, red spheres O atoms on the O-deficient oxide surface, yellow sphere C atom and purple spheres O atoms in the CO₂ molecule.

Figure 3.
CI-NEB result of CO₂ dissociation on Cu₂O (110) surface. “TS” indicates the transition state of the reaction.

Figure 4.

DFT-relaxed geometries and adsorption energies of CO molecule on ideal and defected surfaces: (a) C atom at CuT site of ideal surface, (b) C atom roughly at the H site of ideal surface, (c) C atom at the ShH site of ideal surface, (d) C atom at O vacancy site of O-deficient surface, (e) C atom at CuT site of O-excess surface with additional O at ShH site (f) C atom at CuT site of O-excess surface with additional O at B site. Brown and red spheres represent the Cu and O atoms of native oxide, respectively. Yellow and purple spheres represent the C and O atoms of the adsorbed CO molecule, respectively. Blue spheres represent the additional O atoms on O-excess surfaces.

Figure 5. Total DOS of (a) bulk Cu_2O , (b–e) various Cu_2O (110) surface types with and without adsorbates. The straight dashed line indicates the position of Fermi level calculated by DFT. The gray shaded areas indicate the DOS of bulk or surface structures with no adsorbates. See Fig. 4 for the notations of adsorbate configurations.

Figure 6.

Simulated STM images of (a) ideal Cu_2O (110) surface, (b) O-deficient surface, and O-excess surfaces with an addition O atom at (c) ShH and (d) B sites. Left and right panels show the images generated using -2.0 V and $+1.5\text{ V}$ bias voltages, respectively. Overlaid atomic models indicate the positions of top (brown)- and second (green)-layer Cu atoms, native surface O atoms (red), and additional O atoms (blue).

Figure 7. Simulated STM images of ideal Cu_2O (110) surfaces with adsorbed CO molecules: (a) C atom at CuT site, (b) C atom roughly at the H site of ideal surface, (c) C atom at the ShH site of ideal surface. Left and right panels show the images generated using -2.0 V and $+1.5$ V bias voltages, respectively. Yellow and purple spheres represent the C and O atoms of the adsorbed CO molecule, respectively.

Figure 8. Simulated STM images of CO and CO₂ adsorbed on various defected Cu₂O (110) surfaces: (a) CO and (b) CO₂ adsorbed on O-deficient surface, CO adsorbed on O-excess surfaces with additional O atom at (c) ShH and (d) B sites. Left and right panels show the images generated using -2.0 V and +1.5 V bias voltages, respectively.

Figure 9.

Cu K-edge XANES for bulk Cu_2O . Experimental spectrum was reproduced from Ref. 53. Calculated spectra used a neon-core Cu pseudopotential with energy cutoff of 2850 eV, and an argon-core Cu pseudopotential with energy cutoff of 952 eV, respectively. The simulated spectra are offset horizontally to align with experimental spectra, and offset vertically for presentation.

Figure 10.

Top: calculated Cu K-edge XANES for ideal Cu₂O (110) surface, O-deficient surface and CO₂-adsorbed surface (CO₂O-vac). Bottom: smoothed 2nd derivative of the calculated spectra. The calculated spectra are offset vertically for presentation. Zero energy corresponds to the absorption edge energy of the simulated spectrum for ideal surface. Black dashed line indicates zero of the 2nd derivative.

Table 1

The oxidation states of surface Cu atoms on ideal, O-deficient and CO₂-adsorbed Cu₂O (110) surfaces. The labels of Cu atoms can be found in Fig. 2.

	ideal surface	O-deficient surface	CO ₂ -adsorbed surface
Cu1,2	1.26	0.57	1.13
Cu3,4	1.26	1.21	1.42