

PRF# 714026

**Title: Studies of CO<sub>2</sub> Photoreduction on Cu<sub>2</sub>O at the Single Molecule Level**

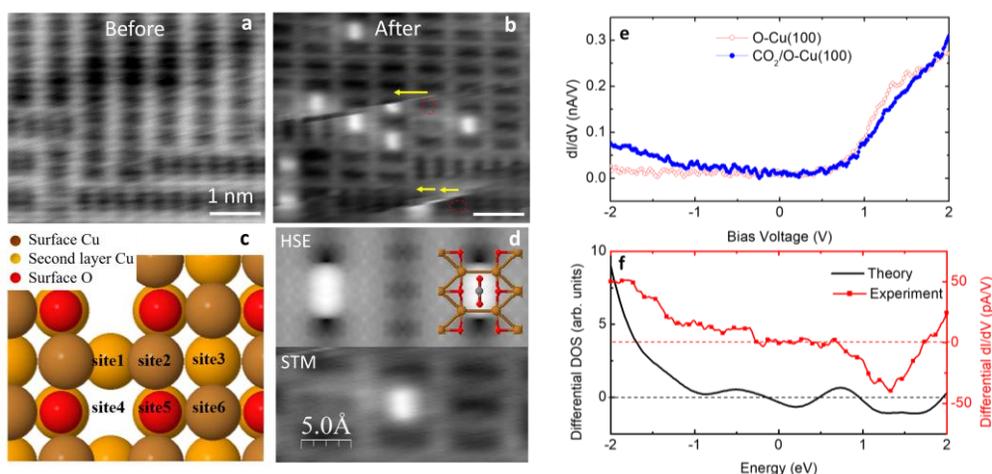
**PI: Dr. Jay Gupta**, Department of Physics, Ohio State University, 191 W. Woodruff Ave, Columbus, OH 43210

**Co-PI: Dr. Aravind Asthagiri**, William G. Lowrie Department of Chemical and Biomolecular Engineering, Ohio State University, 151 W. Woodruff Ave, Columbus, OH 43210

**Motivation and Approach:** This program was focused on a fundamental surface science study of CO<sub>2</sub> adsorption on model copper oxide surfaces. Nanostructured copper oxides have shown unique selectivity for methanol production in photo-electrochemical reduction of CO<sub>2</sub>, but the underlying mechanisms are not well understood. We combined scanning tunneling microscopy (STM) experiments and density functional theory (DFT) calculations to understand adsorption of CO<sub>2</sub> on model surfaces. Experimentally, clean surfaces are prepared in an ultrahigh vacuum, cryogenic environment that enables us to image individual CO<sub>2</sub> molecules and perform tunneling spectroscopy of molecular electronic states. Theoretical calculations were performed using advanced hybrid functionals on server clusters in the Ohio Supercomputing Center. The comparison of experiment and theory helps us to identify the adsorption sites, to estimate diffusion barriers and to probe charge transfer, factors which determine the surface reactivity of CO<sub>2</sub>.

**Accomplishments:** Our initial efforts focused on studying CO<sub>2</sub> molecules on an oxygen adlayer on Cu(100), and we recently published this work in *Surface Science*<sup>1</sup>. This surface represents a model for the initial stages of copper oxidation, and prior work has characterized the ‘missing row’ reconstruction that occurs upon oxidation. The surface was prepared in ultrahigh vacuum (UHV) to minimize contamination and facilitate studies of individual CO<sub>2</sub> molecules. STM experiments were performed at cryogenic temperatures to freeze out thermal motion of CO<sub>2</sub> and to achieve high energy resolution in tunneling spectroscopy. DFT calculations of the surface were performed using the VASP code, with functionals chosen to capture electron exchange and correlation effects, as well as significant van der Waals interactions. DFT results were used to calculate the local density of states and simulate STM images; these were then compared to experimental STM spectroscopy and images.

Figure 1 shows an overview of the insight into CO<sub>2</sub> adsorption we gained in this study. The slab model from our DFT calculations is shown in Fig. 1c to illustrate the missing row reconstruction, characterized by rows of alternating O-Cu-O units, separated by a row of Cu atoms on one side, and a missing row of Cu atoms on the other. This structure is reproduced in our atomic resolution STM images of the surface (Fig. 1a); two domains with a ladder like contrast are observed, rotated by 90deg as expected from the square lattice of Cu(100). There is remarkably little surface contamination, evidenced by the complete lack of molecular adsorbates from residual gas in the UHV chamber. After characterizing the clean surface, CO<sub>2</sub> molecules were introduced into the STM chamber through a precision leak valve at a pressure of 5 x 10<sup>-9</sup> mbar for a very low coverage (<< 1 monolayer). This allowed us to image the same atomic scale area before (Fig. 1a) and after (Fig. 1b) CO<sub>2</sub> adsorption, which facilitates the identification of individual molecules and their adsorption site. Individual CO<sub>2</sub> molecules are imaged as



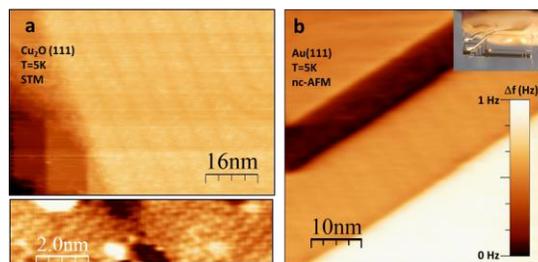
**Figure 1. Summary of STM + DFT study of CO<sub>2</sub> adsorption on O-Cu(100).** (a-b) STM images of the surface before and after adsorption of CO<sub>2</sub> molecules. Individual molecules appear as bright protrusions in the image. (c) Structural model of the surface, with possible adsorption sites as marked. (d) comparison of simulated (top) and experimental (bottom) STM images of a CO<sub>2</sub> molecule. (e) tunneling spectroscopy quantifying CO<sub>2</sub>-induced changes in surface electronic structure (f) comparison of CO<sub>2</sub>-induced changes showing good agreement between experimental spectra (red) and DFT-calculated density of states (black).

dumbbell-shaped bright protrusions, between the ‘rungs’ in the ladder-like contrast of the surface. We performed HSE06-DFT calculations to gain further insight into CO<sub>2</sub> adsorption and compare with our experimental data. Figure 1c shows six possible CO<sub>2</sub> adsorption sites on the missing row reconstructed Cu(100)-O surface examined using DFT. For each adsorption site we performed 45° rotations in the plane to give a total of 24 total configurations. In addition, for select configurations we have also examined CO<sub>2</sub> oriented perpendicular (i.e. upright) to the surface and initially slightly bent CO<sub>2</sub>, but these configurations were found to be not stable. We find that adsorption on the BridgeO site (# 4) is energetically preferred, with a linear configuration of CO<sub>2</sub> oriented along the Cu missing row. DFT-calculated charge densities were then used to simulate STM images, which can be compared with the experimental images. As shown in Fig. 1d, both the DFT simulation and the STM image show that the CO<sub>2</sub> appears with dumbbell-shaped contrast oriented along the missing row.

Experimental tunneling spectra were also compared with theoretical density of states calculations to gain insight into changes in electronic density upon adsorption (Figs. 1e-f). In the experimental spectra (Fig. 1e), the differential change in tunneling current as the bias is swept (dI/dV) is proportional to the local density of states. We can compare spectra taken on the O-Cu(100) surface with spectra taken with the tip positioned directly over the molecule to identify CO<sub>2</sub>-induced electronic structure. Figure 1e shows additional states on CO<sub>2</sub> near negative voltage, and a suppression of states at positive voltage. As confirmed by the corresponding DFT-calculated density of states (Fig. 1f), the large gap between occupied and empty molecular orbitals in CO<sub>2</sub> is preserved upon adsorption, which leads to relatively featureless spectra in the range we could measure experimentally. However, we do find good agreement with the DFT- calculated density of states over this range, from which we learn that the negative voltage rise reflects the tail of the highest occupied CO<sub>2</sub> molecular orbital, while the suppression at positive voltage is associated with CO<sub>2</sub>-induced reduction in Cu substrate states.

The consistent agreement between the experimental STM data and the DFT calculations helped us confirm a picture of CO<sub>2</sub> physisorption on the O-Cu(100) surface. DFT-calculated adsorption energies, vibrational frequencies and diffusion barriers indicate that CO<sub>2</sub> weakly sticks on the surface, and thus would be expected to be quite mobile on the surface at elevated temperatures. We find relatively little change in the CO<sub>2</sub> molecule upon physisorption, which suggests that lower-coordinated step edge or defect sites are more likely to catalyze CO<sub>2</sub> surface chemistry.

**Future Plans:** We will continue this work under a recently-funded NSF award (CHE-1809837). Our initial focus is to study CO<sub>2</sub> adsorbed on monolayer/multi-layer films of Cu<sub>2</sub>O, which more closely mimics the surfaces found in copper oxide catalysts. The advantage of this method is that we can controllably grow thin films of Cu<sub>2</sub>O with monolayer control, allowing us to study how the electronic structure of the films and CO<sub>2</sub> adsorption depend on the thickness spanning single monolayers up to more bulk-like few nm-scale films. We have recently grown monolayer Cu<sub>2</sub>O on Cu(100), and surprisingly found that Cu<sub>2</sub>O grows in the incommensurate hexagonal (111) lattice rather than the square lattice dictated by the substrate. Strain with the surface may produce a periodic series of dark stripes in the image. Now that we have demonstrated successful growth of the surface, we will deposit CO<sub>2</sub> molecules and study molecular adsorption, while also developing theoretical models of the Cu<sub>2</sub>O(111)/Cu(100) surface structure. We will also continue to develop so-called non-contact AFM methods that are suitable for imaging CO<sub>2</sub> on thicker, more insulating copper oxide surfaces. Using the qPlus AFM sensor, we have recently achieved the first nc-AFM images of the herringbone reconstruction on a test Au(111) sample (Fig. 2b). The combination of STM and nc-AFM will extend our ability to study CO<sub>2</sub> adsorption on both conducting and insulating surfaces.



**Figure 2. Future plans** (a) STM images of monolayer Cu<sub>2</sub>O(111) films grown on Cu(100). (b) non-contact AFM image of a Au(111) surface, showing several steps on the surface, and the characteristic herringbone reconstruction.

<sup>i</sup> Tjung, S. J., Zhang, Q., Repicky, J. J., Yuk, S. F., Nie, X., Santagata, N. M., Asthagiri, A., and Gupta, J. A. “STM and DFT Studies of CO<sub>2</sub> Adsorption on O-Cu(100) Surface” *Surface Science* 679, (2019): 50–55. doi:10.1016/J.SUSC.2018.08.013