Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Determining Intrinsic Stark Tuning Rates of Adsorbed CO on Copper Surfaces

Xiaoxia Chang[1,2,3], Haocheng Xiong[1,2,4], Yifei Xu[1,2], Yaran Zhao[3], Qi Lu[4,*] and Bingjun Xu[1,2,3,*]

[1]College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China
[2] Beijing National Laboratory for Molecular Sciences, Beijing, 100871, China
[3]Center for Catalytic Science and Technology, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States
[4]State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

*Corresponding authors: luqicheme@mail.tsinghua.edu.cn, b_xu@pku.edu.cn

Methods

Preparation of SEIRA active Au films. Before the deposition of Au film, the silicon ATR crystal was first washed with the aqua regia solution to remove any left-over metals. Then the prism was polished using a slurry of 0.05 µm Al_2O_3 and sonicated in acetone and DI-water, respectively. After that, the silicon prism was dired with air and then immersed in NH_4F solution (40%, Sigma-Aldrich) for 150 s to create a hydrogen-terminated surface. Then the silicon prism was immersed into a mixture of 2 wt% HF aqueous solution (99%, Sigma-Aldrich) and Au plating solution under 55 °C water bath for 10 min to chemically deposit Au film onto the reflecting surface of this prism. The Au plating solution is prepared by mixing 5.75 mM $NaAuCl_4 \cdot 2H_2O$ (99%), 0.025 M NH_4Cl (99.99%), 0.025 M $Na_2S_2O_3 \cdot 5H_2O$ (98%), 0.075 M Na_2SO_3 (98%), and 0.026 M NaOH (99%). All chemicals used in the plating solution were purchased from Sigma-Aldrich. After the deposition, the obtained Au film on silicon prism was rinsed with DI-water and dried with air. In order to obtain surface enhanced infrared absorption activity, the Au film was treated under cyclic voltammetry scans from -0.2 to 1.6 V_{RHE} for 20 cycles in 0.1 M $NaHCO_3$ (prepared by purging CO_2 into Na_2CO_3 (≥99.9999%, Fluka) overnight until the pH reached 6.8). After the pre-activation, CO was introduced into the electrolyte under cyclic voltammetry scans and the CO band on Au was monitored by SEIRAS. The only appearance of a single band at ~2100 cm^{-1} indicates the good activation and cleanliness of the obtained Au film.

Preparation of oxide-derived Cu (OD-Cu) electrode. The OD-Cu electrode was prepared through the reduction of pre-deposited Cu_2O film on the Au film. The Cu_2O film was prepared via an electrodeposition method as described previously.[1,2] Briefly, the electrolytic aqueous bath contains 0.4 M cupric sulfate (99.99%, Sigma-Aldrich) and 3 M lactic acid and was adjusted to pH 11.5 by adding sodium hydroxide (99.99%, Sigma-Aldrich). It should be noted that L-lactic acid (98%, Alfa Aesar, shown in Figure S5) and DL-lactic acid (90%, Sigma-Aldrich, shown in Figure 1) were employed and compared in this work. In the synthesis, the DL-lactic acid (Figure 1) was replacd by L-lactic acid (Figure S5). The electrodeposition was conducted potentiostatically at -0.4 V versus Ag/AgCl in a typical three-electrode system using Au film as the working electrode (WE), a graphite rod as the counter electrode (CE) and the saturated Ag/AgCl (BASi) as the reference electrode (RE). The electrodeposition was carried out in the 60 °C water bath and controlled by deposition charge amount of 100 mC onto 1 cm^2 substrate. Prior to the spectroscopic experiment, the Cu_2O electrode was reduced at a constant current density of -500 μA cm^{-2} for 5 min in 0.1 M $NaHCO_3$. The obtained OD-Cu film was then rinsed with DI-water and dried with air.

Preparation of chemically deposited Cu film (Chem-Cu) and Chem-Cu-DC electrodes. The Chem-Cu electrode chemically deposited on silicon crystal was prepared using a previous method.[3] The cleaned silicon crystal's reflecting surface was immersed in 40% aqueous solution of NH_4F for 1 min to create a hydride-terminated surface. The crystal was then immersed in a copper seeding solution (0.5 wt% hydrofluoric acid and 750 μM $CuSO_4$) for 2 min, followed by a plating solution (0.25 M HCHO, 0.02 M $CuSO_4$, 20 mM Na_2EDTA and 0.3 mM 2,2-bipyridine, pH value 12, temperature 55 °C) for 5-6 mins. The resulting surface was gently rinsed with water, dried by air and ready to be used. The Chem-Cu-DC electrode was prepared by scraping the Chem-Cu film off Si substrate and dropcasting the catalyst ink onto the SEIRA active Au film. The ink contains 10 mg of Chem-Cu powder and 0.25 mL isopropanol (Fisher Chemicals). Then the obtained Chem-Cu-DC electrode was dried at 55 °C for 1 h.

Preparation of dendritic Cu (Den-Cu) and Cu microparticles (Cu MPs) electrodes. The Den-Cu and Cu MPs electrodes were prepared through dropping the inks of Den-Cu and Cu MPs onto the obtained Au flim. First, 100 mg of commercial dendritic Cu powder (<45 μm, 99.7% trace metals basis, Sigma-Aldrich) or spherical Cu powder (0.5-1.5 μm, 99% trace metals basis, Alfa Aesar) was dispersed in 2.5 mL of isopropanol and then 15 μL of Nafion solution (10 wt%, Fuel Cell Store) was added into the mixture. After sonicating for 30 min, 50 μL of the suspension liquid was uniformly dropped onto 1 cm^2 of the Au film. Then the obtained electrode was dried at 55 °C for 1 h.

Preparation of Pt and Pt-DC electrodes. Polycrystalline Pt film was deposited on Si crystal by an electroless chemical plating method as described before.[4,5] First of all, a Pd seed layer was directly deposited on the reflecting plane of the Si prism in order to improve the adhesion of Pt film.[6] The Pd deposition solution in water was made up of 0.23 mM $PdCl_2$ (99.999%, Alfa Aesar), 0.014 M HCl, 0.28 M HF (48%, 99.99% metals basis, Sigma Aldrich), and 0.76 M NH_4F (40%, Sigma-Aldrich). Before depositing Pd seed layer, the Si crystal was first immersed into 40% NH_4F for 1 min and 45 s to make a hydrogen-terminated surface. The it was immersed in the Pd plating solution at 50 °C for 3 min to obtain the Pd seed layer, after which it was rinsed using DI water, dried with blowing air and sintered at 200 °C for 30 min in a vacuum evacuated tube furnace. The Pt plating solution consists two separate parts: (1) 0.01 M $H_2PtCl_6·6H_2O$ (Sigma Aldrich) aqueous solution; (2) 0.3 M NH_3 (30%, Fisher Scientific), 0.036 M $HONH_3Cl$ (99.999% Aldrich), and 0.04 M $N_2H_4·H_2O$ (98%, Sigma Aldrich). These two solutions were mixed by the volume ratio of 1:1 immediately before Pt deposition. Then the Pd-seeded Si prism was immersed into the mixed Pt plating solution at 60 °C for several minutes, during which a voltmeter was used to check the conductivity of the film until a conductive Pt film was achieved. Then the obtained Pt film was rinsed with DI water and dried with blowing air. The Pt-DC electrode was prepared by scraping the Pt film off Si substrate and dropcasting the ink onto the SEIRA active Au film. The ink contains

10 mg of Pt powder and 0.25 mL isopropanol. Then the obtained Pt-DC electrode was dried at 55 °C for 1 h.

Preparation of electrolytes. Sodium carbonate (99.999%) was supplied by Merck. Sodium phosphate (99.5%) was purchased from Fisher Chemical. Sodium hydroxide (99.9%) and perchloric acid (70%, 99.999% trace metals basis) were purchased from Sigma-Aldrich. The electrolytes employed in this work were all pre-electrolyzed at a constant reducing current of -10 mA for 24 h to deposit most of the metal impurities onto the counter electrode of a Cu foil (Sigma-Aldrich, 99.998%). A graphite rod was used as the counter electrode for 0.1 M $HClO_4$.

Materials characterization. Scanning electron microscopy (SEM) images were obtained on a field emission electron microscope (SEM/FIB Auriga 60, ZEISS).

In-situ surface enhanced infrared absorption spectroscopy (SEIRAS) test. In-situ SEIRAS tests were conducted in a home-designed spectro-electrochemical cell with a three-electrode configuration as shown in Figure S1. The obtained metal film deposited on Si ATR crystal was used as working electrode, a graphite rod as the counter electrode, and a saturated Ag/AgCl (BASI) as the reference electrode. The graphite rod was used as the counter electrode in order to avoid any metal contamination as described in previous study.[7] The cell was integrated into the Agilent Technologies Cary 660 FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector. During the test, CO gas was kept bubbling into the electrolyte and the system was mechanically stirred. The potential on the cell was supplied by a Solartron 1260/1287 system for electrochemical measurements. The spectra presented in this work correspond to 64 coadded scans.

Supplementary Figures

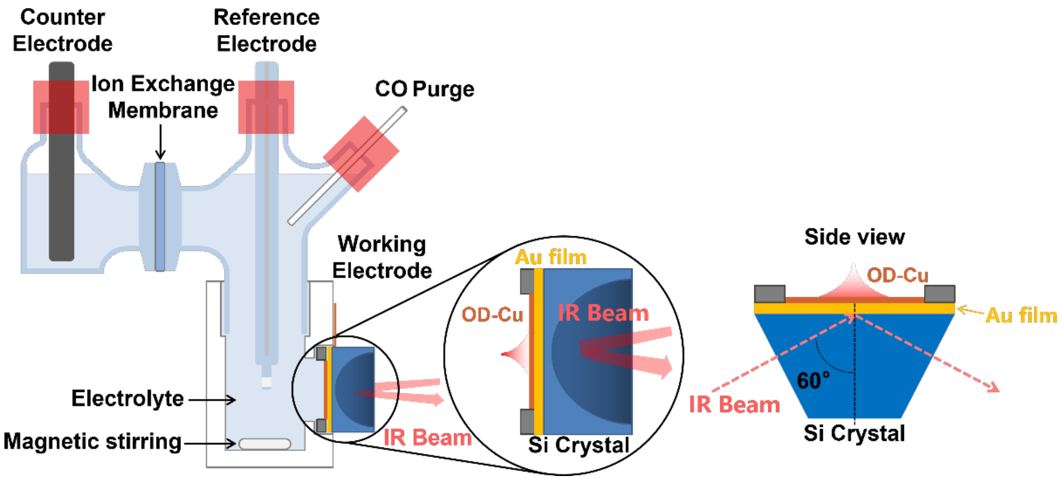

Figure S1. Schematic of the spectro-electrochemical cell with stirring function for in-situ SEIRAS experiments. The cell consists of two compartments that are separated by a piece of Nafion ion exchange membrane. The side views of the working electrode from different angles are also shown.

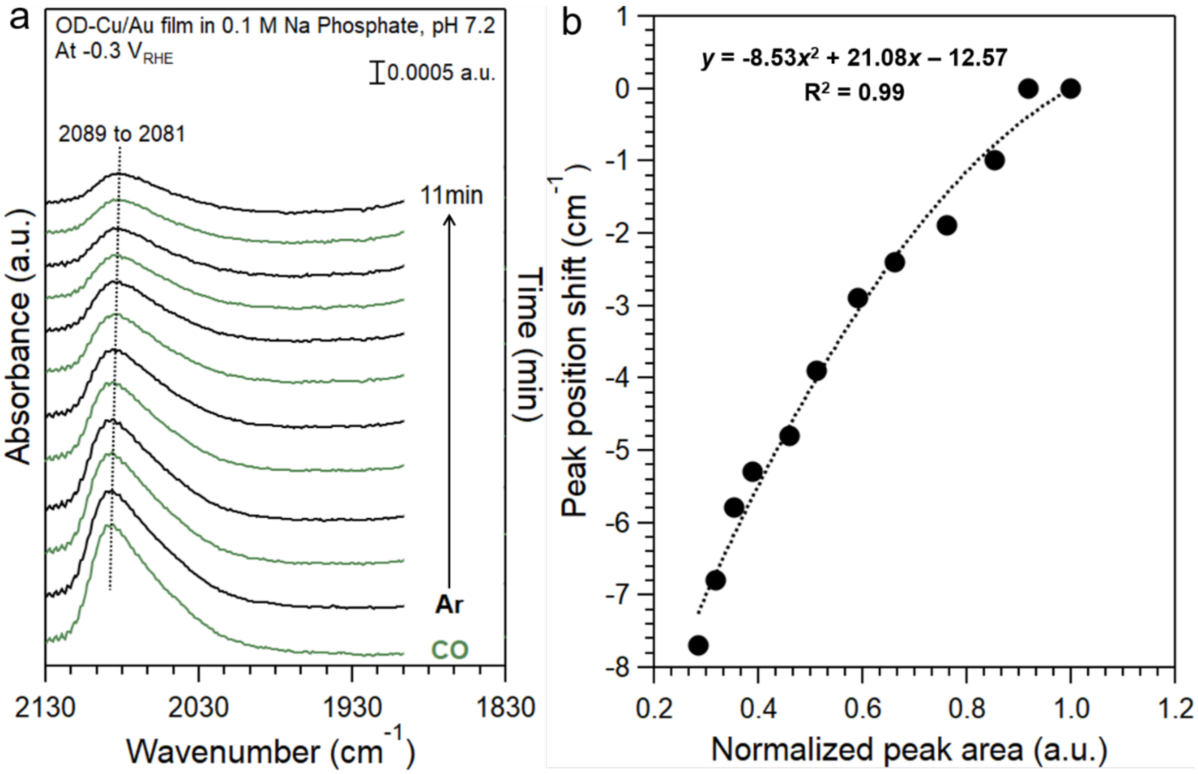

Figure S2. (a) In-situ SEIRAS study on the peak area dependence of CO band frequency through switching the bubbling gas to Ar on OD-Cu at -0.3 V$_{RHE}$ in 0.03 M NaH_2PO_4 + 0.035 Na_2HPO_4 (pH = 7.2). (b) The peak position shift from that under CO as a function of the peak area. The second-order polynomial fitting of the point data is shown as dashed line. The spectrum resolution is set at 2 cm^{-1} for an accurate calibration.

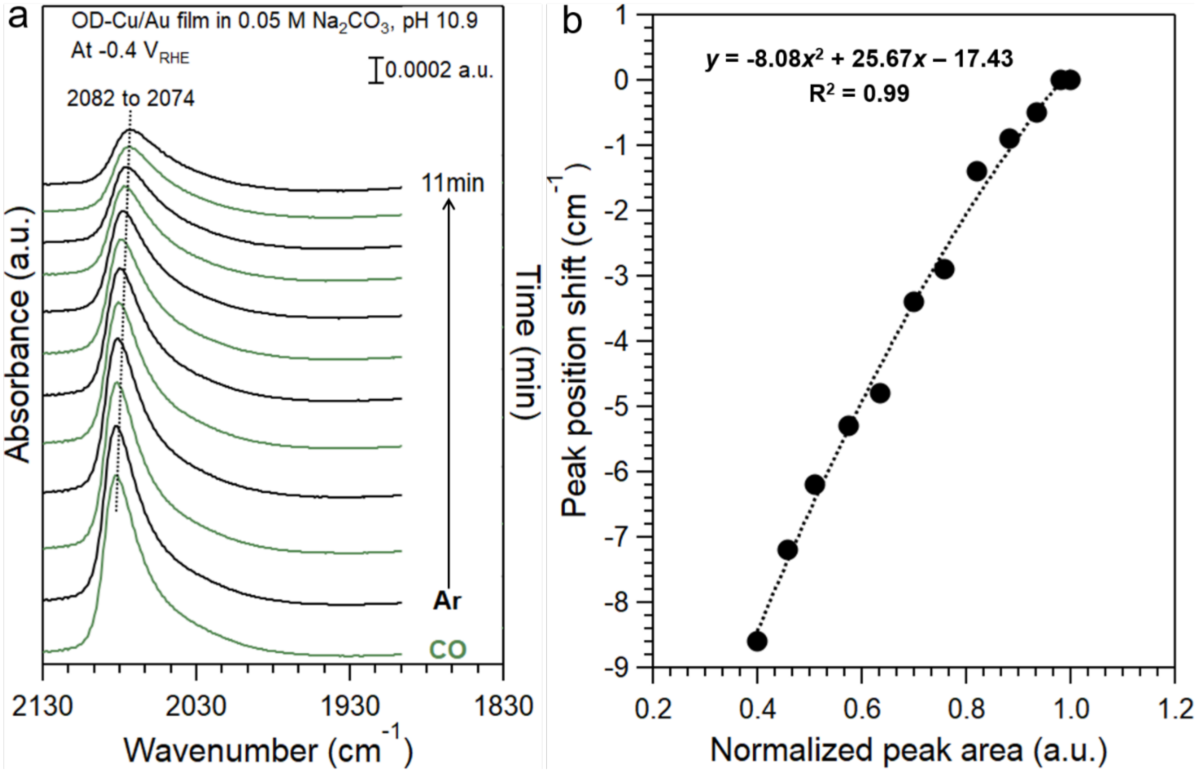

Figure S3. (a) In-situ SEIRAS study on the peak area dependence of CO band frequency through switching the bubbling gas to Ar on OD-Cu at -0.4 V$_{RHE}$ in 0.05 M Na$_2$CO$_3$ (pH = 10.9). (b) The peak position shift from that under CO as a function of the peak area. The second-order polynomial fitting of the point data is shown as dashed line. The spectrum resolution is set at 2 cm^{-1} for an accurate calibration.

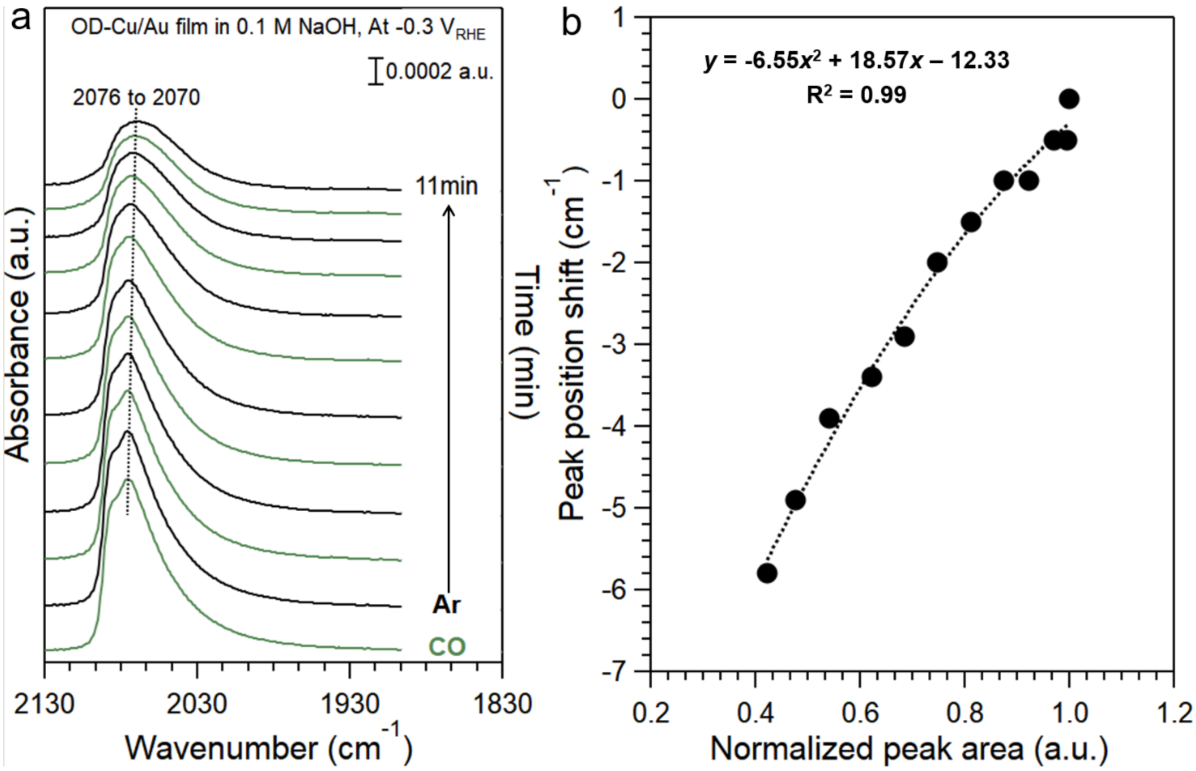

Figure S4. (a) In-situ SEIRAS study on the peak area dependence of CO band frequency through switching the bubbling gas to Ar on OD-Cu at -0.3 V_{RHE} in 0.1 M NaOH (pH = 12.9). (b) The peak position shift from that under CO as a function of the peak area. The second-order polynomial fitting of the point data is shown as dashed line. The spectrum resolution is set at 2 cm^{-1} for an accurate calibration.

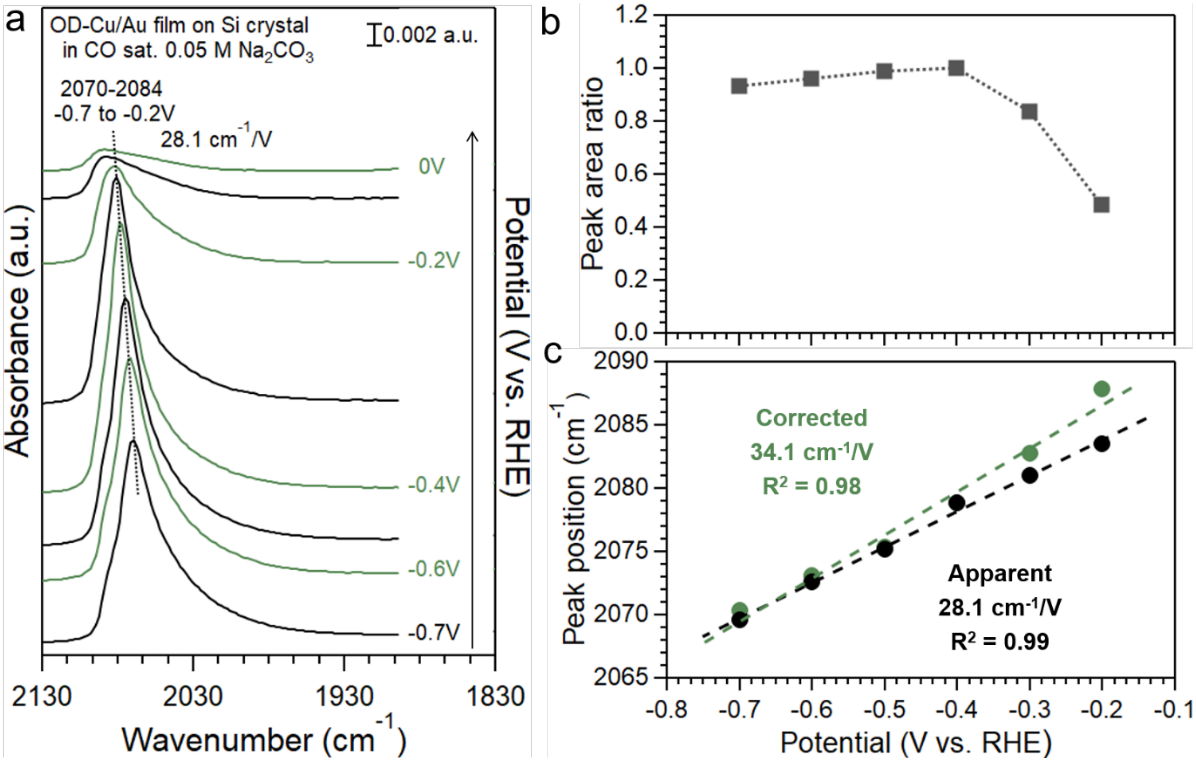

Figure S5. (a) In-situ SEIRA spectra of CO adsorption on OD-Cu (prepared using L-lactic acid instead of DL-lactic acid) in 0.05 M Na_2CO_3 (pH = 10.9) at potentials indicated in the figure. The spectra were collected at constant potentials with 0.1 V intervals in the anodic direction from the -0.7 to 0 V_{RHE}. (b) The normalized peak area of the CO adsorption bands as a function of potential. (c) The apparent (black) and corrected (green) potential dependence of CO band frequency. Stark tuning rates are determined through the linear fits of the point data between -0.7 and -0.2 V_{RHE}.

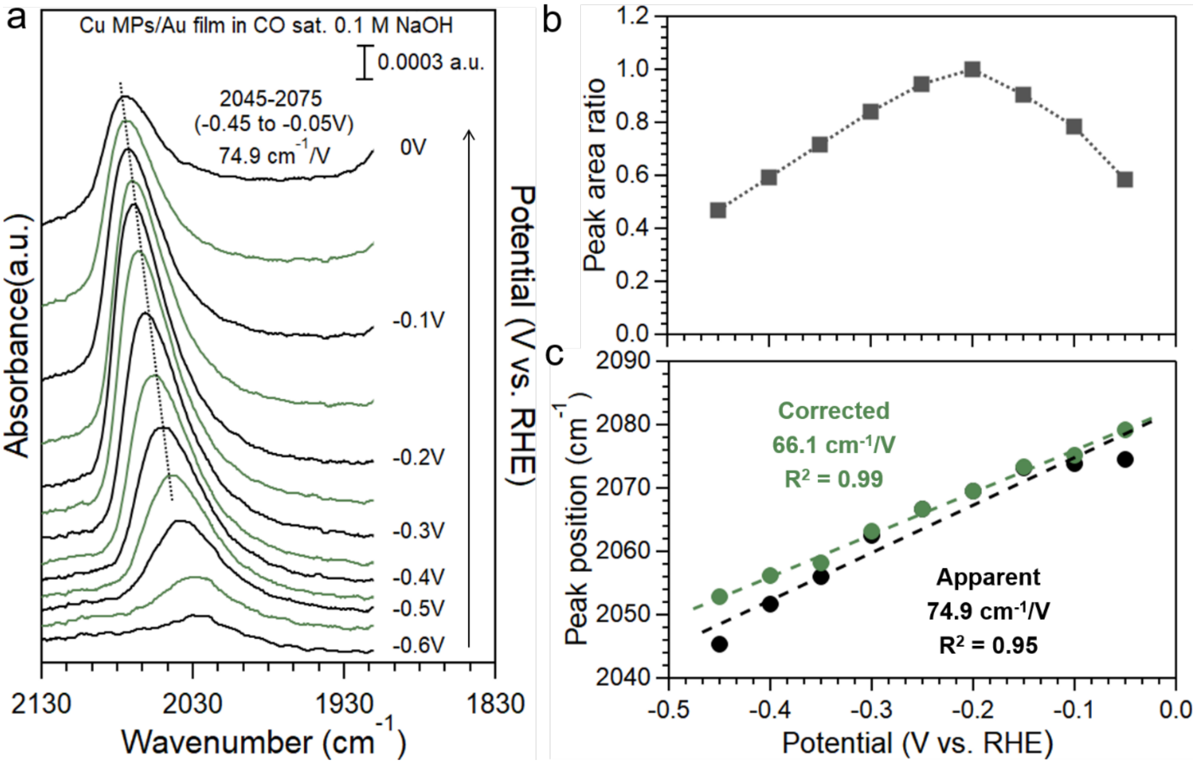

Figure S6. (a) In-situ SEIRA spectra of CO adsorption on Cu MPs in 0.1 M NaOH (pH = 12.9) at potentials indicated in the figure. The spectra were collected at constant potentials with 0.05 V intervals in the anodic direction from the -0.6 to 0 V_{RHE}. (b) The normalized peak area of the CO adsorption bands as a function of potential. (c) The apparent (black) and corrected (green) potential dependence of CO band frequency. Stark tuning rates are determined through the linear fits of the point data.

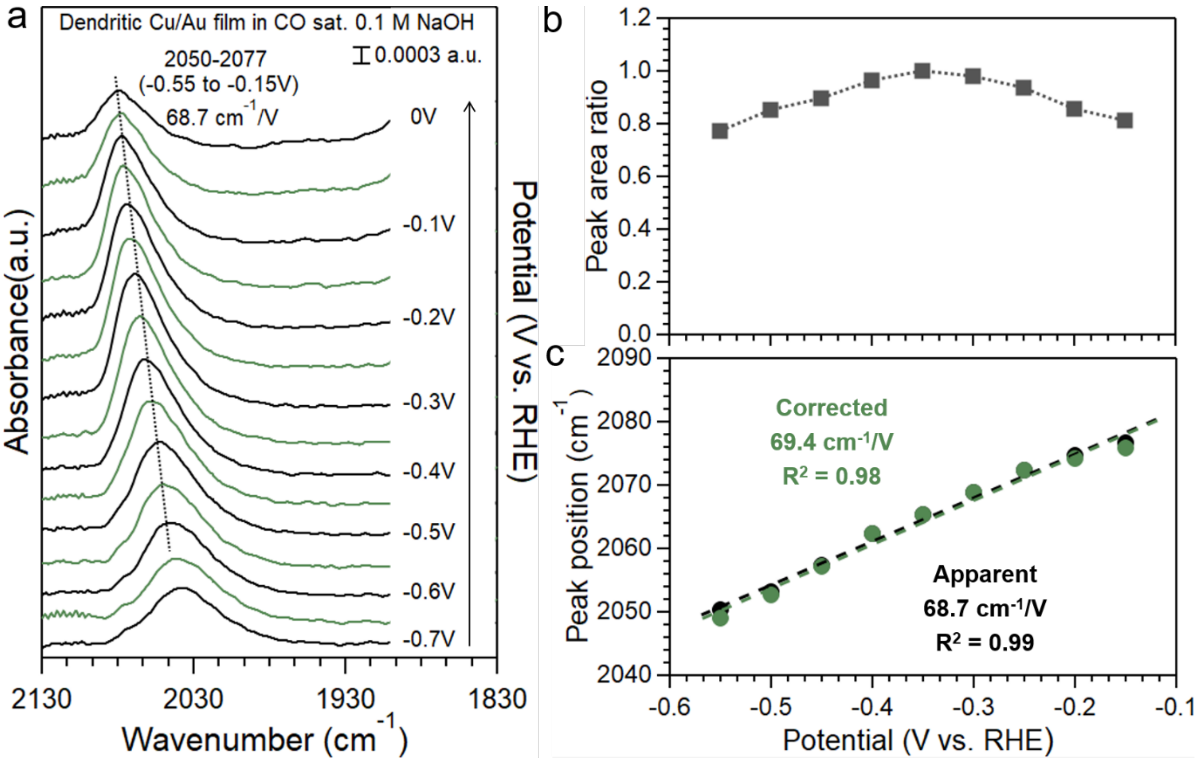

Figure S7. (a) In-situ SEIRA spectra of CO adsorption on Den-Cu in 0.1 M NaOH (pH = 12.9) at potentials indicated in the figure. The spectra were collected at constant potentials with 0.05 V intervals in the anodic direction from the -0.7 to 0 V_{RHE}. (b) The normalized peak area of the CO adsorption bands as a function of potential. (c) The apparent (black) and corrected (green) potential dependence of CO band frequency. Stark tuning rates are determined through the linear fits of the point data.

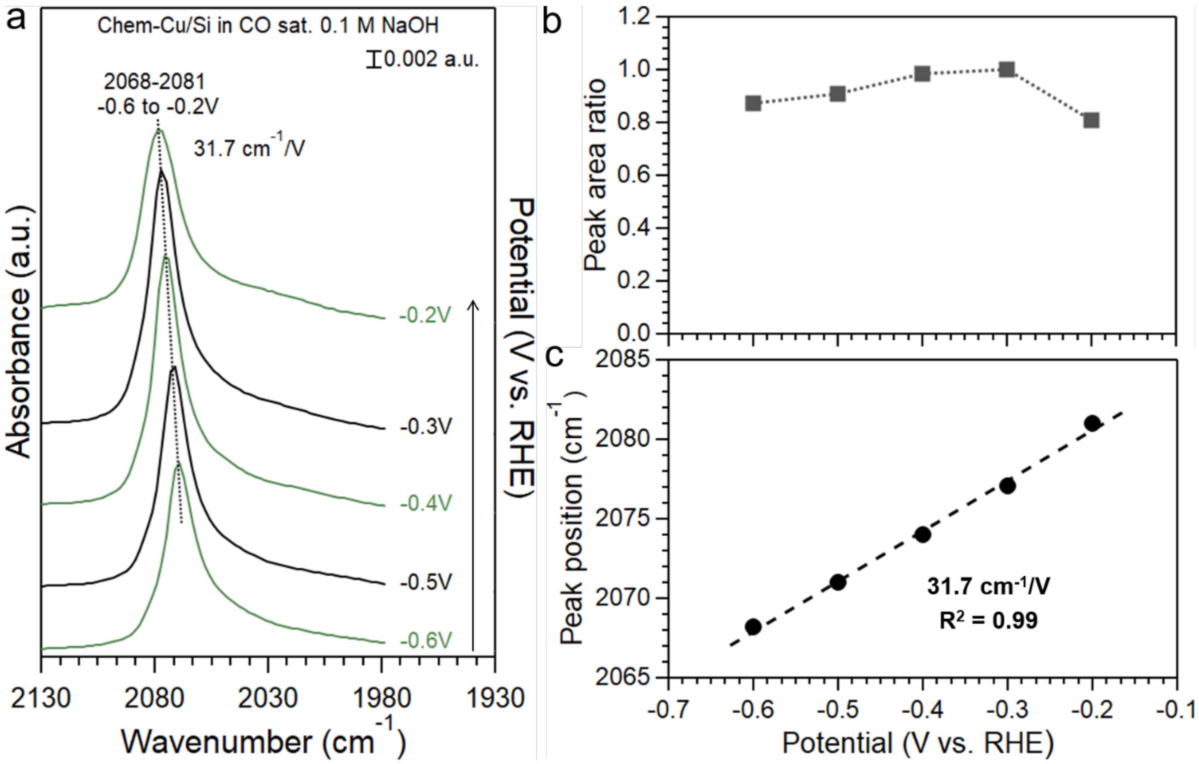

Figure S8. (a) In-situ SEIRA spectra of CO adsorption on Chem-Cu film in 0.1 M NaOH (pH = 12.9) at potentials indicated in the figure. The spectra were collected at constant potentials with 0.1 V intervals in the anodic direction from the -0.6 to -0.2 V_{RHE}. (b) The normalized peak area of the CO adsorption bands as a function of potential. (c) The potential dependence of CO band frequency. Stark tuning rate on Chem-Cu film is determined through the linear fit of the point data and unnecessary to be corrected due to the barely changed peak intensity.

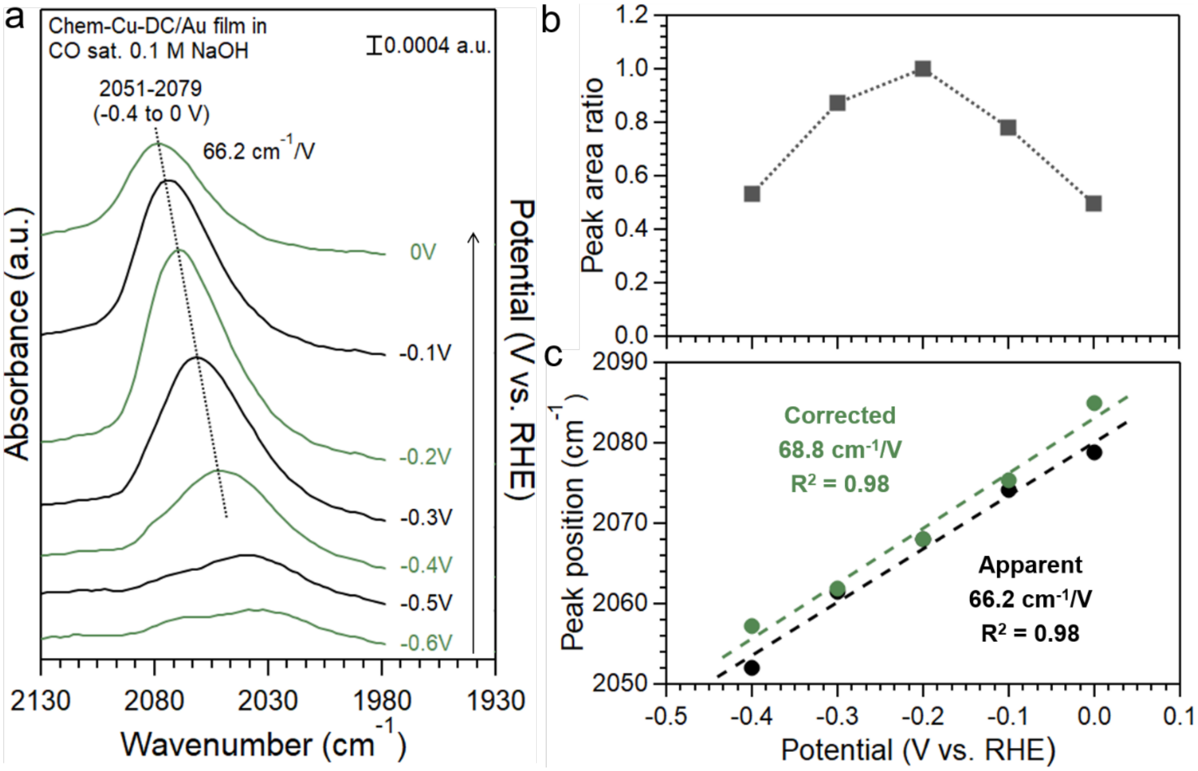

Figure S9. (a) In-situ SEIRA spectra of CO adsorption on Chem-Cu-DC in 0.1 M NaOH (pH = 12.9) at potentials indicated in the figure. The Chem-Cu-DC was obtained by scraping the Chem-Cu film in Figure S8 off the Si substrate and dropcasting onto Au film. The spectra were collected at constant potentials with 0.1 V intervals in the anodic direction from the -0.6 to 0 V_{RHE}. (b) The normalized peak area of the CO adsorption bands as a function of potential. (c) The apparent (black) and corrected (green) potential dependence of CO band frequency. Stark tuning rates are determined through the linear fits of the point data.

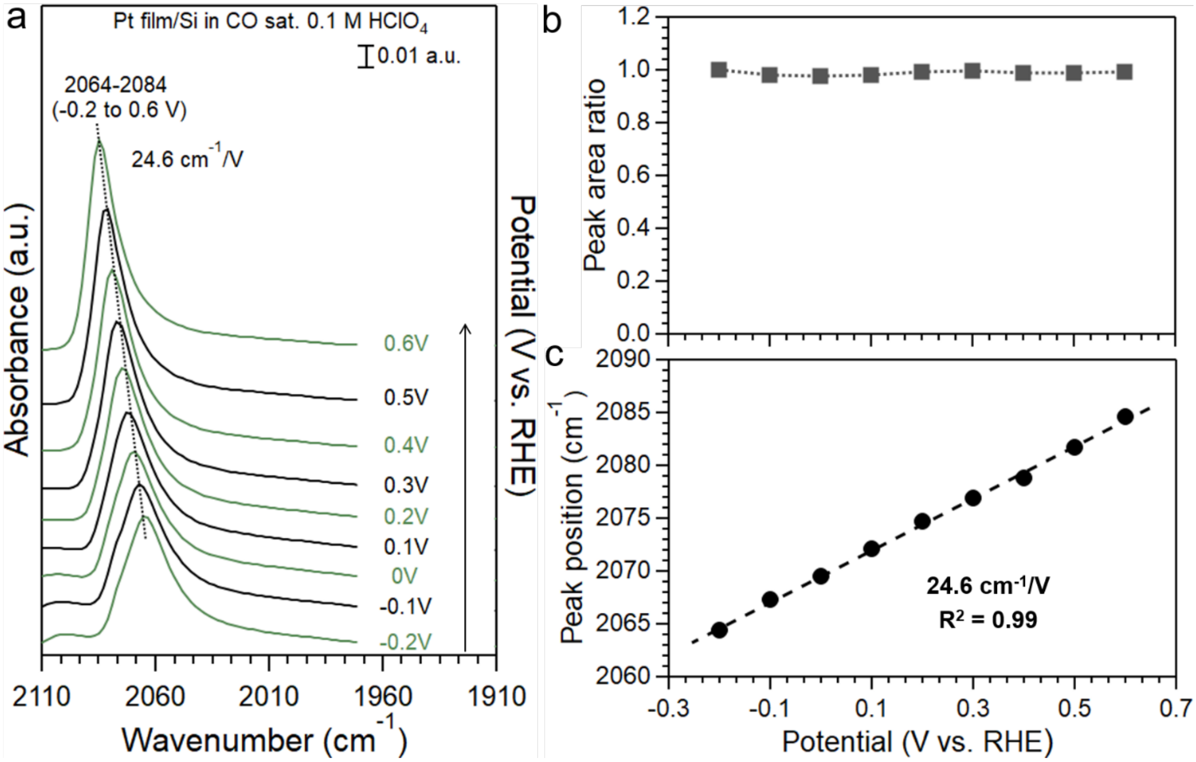

Figure S10. (a) In-situ SEIRA spectra of CO adsorption on Pt film in 0.1 M $HClO_4$ (pH = 1.2) at potentials indicated in the figure. The spectra were collected at constant potentials with 0.1 V intervals in the anodic direction from the -0.2 to 0.6 V_{RHE}. (b) The normalized peak area of the CO adsorption bands as a function of potential. (c) The potential dependence of CO band frequency. Stark tuning rate on Pt film is determined through the linear fit of the point data and unnecessary to be corrected due to the barely changed peak intensity.

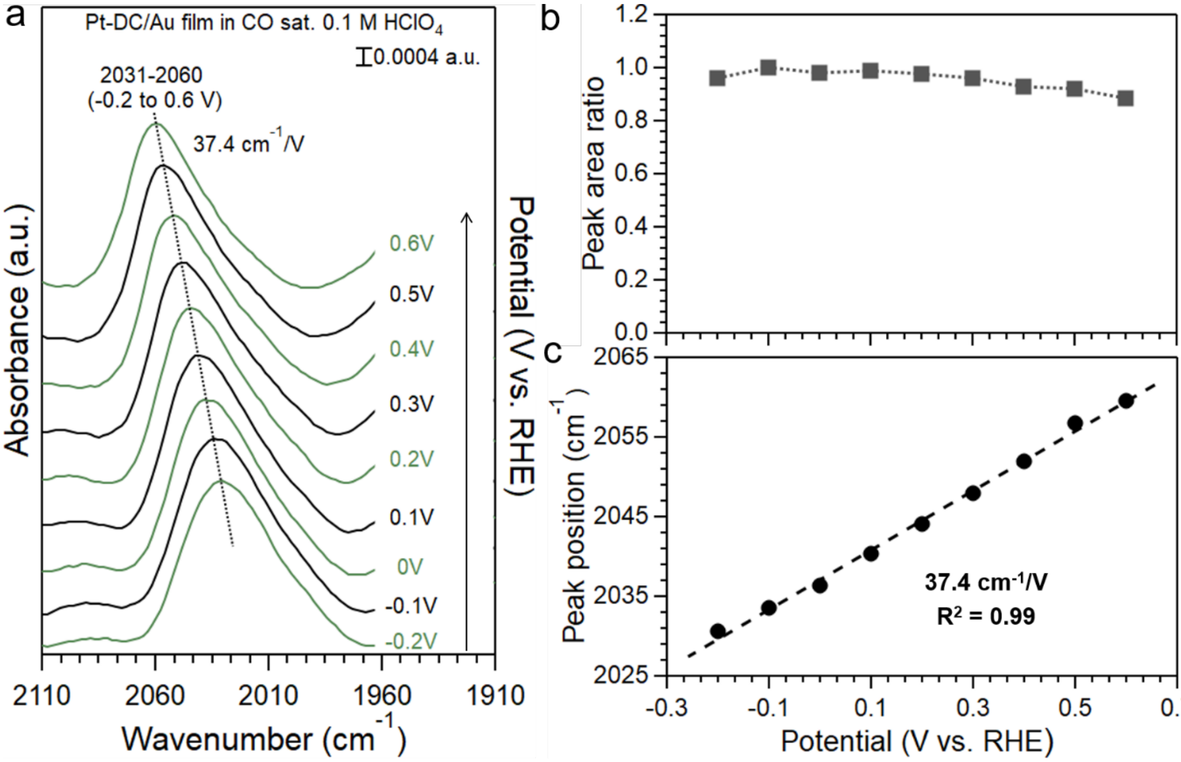

Figure S11. (a) In-situ SEIRA spectra of CO adsorption on Pt-DC in 0.1 M $HClO_4$ (pH = 1.2) at potentials indicated in the figure. The Pt-DC was obtained by scraping the Pt film in Figure S10 off the Si substrate and dropcasting onto Au film. The spectra were collected at constant potentials with 0.1 V intervals in the anodic direction from the -0.2 to 0.6 V_{RHE}. (b) The normalized peak area of the CO adsorption bands as a function of potential. (c) The potential dependence of CO band frequency. Stark tuning rate on Pt-DC is determined through the linear fit of the point data and unnecessary to be corrected due to the barely changed peak intensity.

References

1 X. Chang, A. Malkani, X. Yang and B. Xu, *J. Am. Chem. Soc.*, 2020, **142**, 2975-2983.

2 X. Chang, T. Wang, P. Zhang, Y. Wei, J. Zhao and J. Gong, *Angew. Chem. Int. Ed.*, 2016, **55**, 8840-8845.

3 A. S. Malkani, M. Dunwell and B. Xu, *ACS Catal.*, 2019, **9**, 474-478.

4 A. Miki, S. Ye and M. Osawa, *Chem. Commun.*, 2002, 1500-1501.

5 X. Yang, J. Nash, N. Oliveira, Y. Yan and B. Xu, *Angew. Chem. Int. Ed.*, 2019, **58**, 17718-17723.

6 S. Karmalkar and J. Banerjee, *J. Electrochem. Soc.*, 2019, **146**, 580-584.

7 M. Dunwell, X. Yang, Y. Yan and B. Xu, *J. Phys. Chem. C*, 2018, **122**, 24658-24664.