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Supplementary information for

Surface Enhanced Spectroscopic Investigations of Impact of Cations on Electrochemical Interfaces

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Materials and Methods

Pt and Au film electrode preparation. Pt film electrodes on top of a thin Pd underlayer were prepared using an electroless chemical plating method on an undoped Si prism using a modified deposition procedure outlined by Miki et. al.[1, 2] The Si prism was first polished using 0.05 µm alumina slurry, then rinsed using double deionized-distilled water (Barnstead Mega-Pure Water Purification System) and acetone successively to remove alumina residue. Following cleaning, a Pd seed layer was then deposited directly on the reflecting plane of the Si prism in order to improve adhesion of the Pt overlayer.[3] The Pd deposition solution consisted of 0.23 mM $PdCl_2$ (99.999%, Alfa Aesar) + 0.014 M HCl (36.5-38% HCl, Fischer Scientific) + 0.28 M HF (48%, 99.99% metals basis, Sigma Aldrich) + 0.76 M NH_4F (40%, Fluka) in distilled water. The reflecting plane of the Si crystal was first immersed in 40% NH_4F for 1 min and 45 s in order to create a hydrogen-terminated Si surface. The crystal was then immersed in a room temperature Pd plating solution for 6 min to deposit the Pd seed layer. The Si crystal is then rinsed with distilled water and dried using air. The Pd-seeded Si prism was then sintered at 200 °C for 30 min in a vacuum evacuated tube furnace. After sintering, the Si prism was rinsed and the Pd-seeded reflecting plane of the prism was immersed in the Pt plating solution at 60 °C for ~2 min. The Pt plating solution consisted of two separate solutions. The first solution, containing the Pt salt, is 0.01 M $H_2PtCl_6 \cdot 6H_2O$ (Sigma Aldrich). The second solution, used to adjust solution pH and stabilize the Pt mixture, is 0.3 M NH_3 (30%, Fischer Scientific) + 0.036 M $HONH_3Cl$ (99.999%, Aldrich) + 0.04 M $N_2H_4 \cdot H_2O$ (98%, Sigma Aldrich). The two solutions were mixed in a 1:1 (vol) ratio immediately before Pt deposition. A detailed procedure for preparation of the SEIRAS-active Au film is given in our previous work.[4]

Experimental procedures. ATR-SEIRAS experiments were conducted in a two-compartment spectroelectrochemical cell as described previously.[4] The working electrode was the Pt or Au films described in the previous section. A Pt wire counter electrode was used for all experiments on Pt film working electrodes, and a graphite rod was used for all experiments using an Au film working electrode in order to present contamination of the Au working electrode by Pt deposition from the counter electrode. A Ag/AgCl (3.0 M KCl, BASi) reference electrode was used in the working electrode compartment for all experiments. The working and counter electrode compartments were separated using a Nafion proton exchange membrane. Spectra were collected during cyclic voltammetry and potentiostatic experiments in 0.1 M $LiClO_4$ (99+%, Arcos Organics), $NaClO_4$ (99+%, Arcos Organics), $KClO_4$ (> 99.99% metals basis, Sigma Aldrich), TMACl (≥ 98%, Sigma Aldrich), TEACl (25% TEAOH, Alfa Aesar + 36.5-38% HCl, Fischer Scientific), TPACl (40% TPAOH, SACHEM + 36.5-38% HCl, Fischer Scientific), and TBACl (40% TBAOH, SACHEM + 36.5-38% HCl, Fischer Scientific) under continuous CO purge (Matheson). All spectroscopic and electrochemical data were collected using an Agilent Technologies Cary 660 FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector and a Pike Technologies VeeMAX II ATR accessory coupled with a Solartron SI 1260/1287 system for electrochemical measurements.

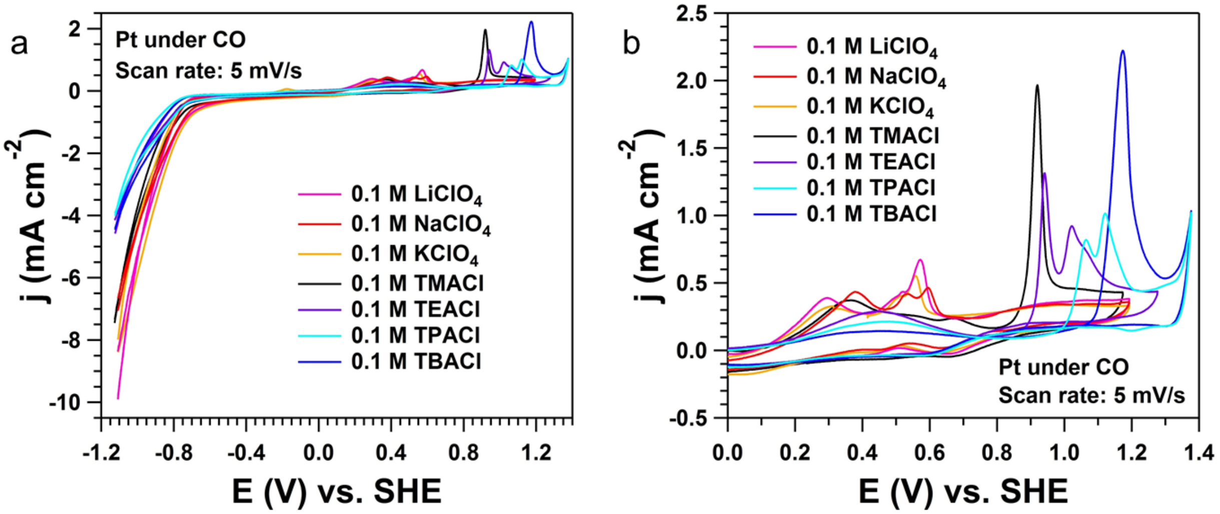

Fig. S1 (a) Cyclic voltammograms at 5 mV s^{-1} in 0.1 M solutions of $LiClO_4$ (pink), $NaClO_4$ (red), $KClO_4$ (orange), TMACl (black), TEACl (purple), TPACl (light blue), TBACl (blue) under continuous CO purge corresponding to the spectra in main text Fig. 1 and Figs. S4-S9. (b) Zoom of the CO oxidation region of (a). The delayed CO oxidation in the tetraalkylammonium chloride solutions is likely due to chloride poisoning of the Pt surface at high potentials.

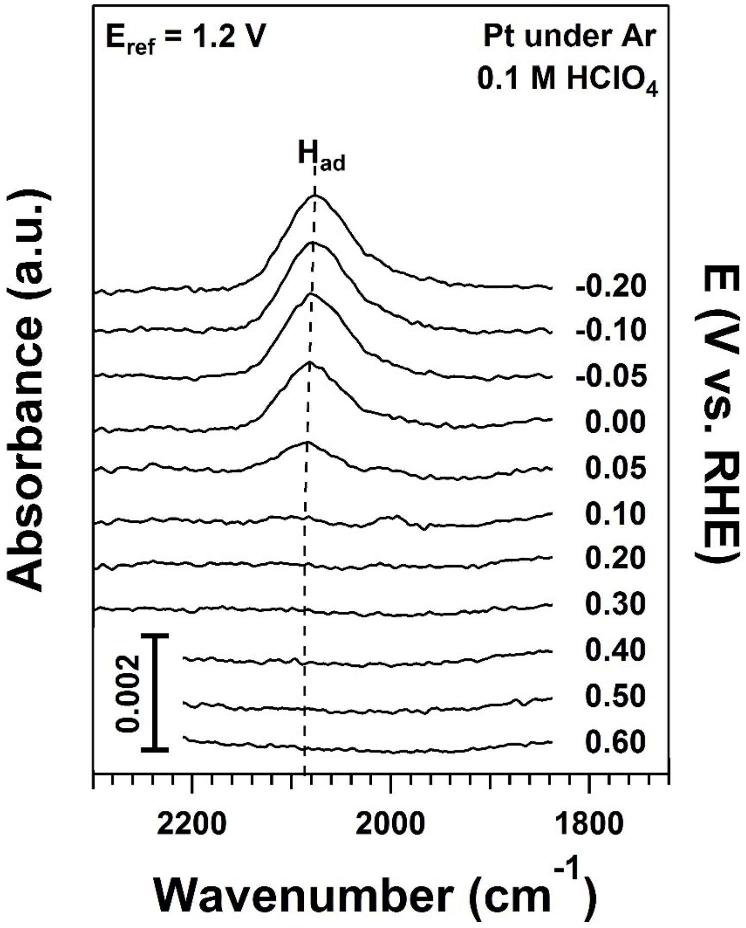

Fig. S2 ATR-SEIRA spectra (4 cm^{-1} resolution, 64 co-added scans) during potential steps from 0.6 V to -0.2 V on chemically deposited Pt film electrode in 0.1 M $HClO_4$ under 1 atm Ar. Reference spectrum collected at 1.2 V vs. RHE.

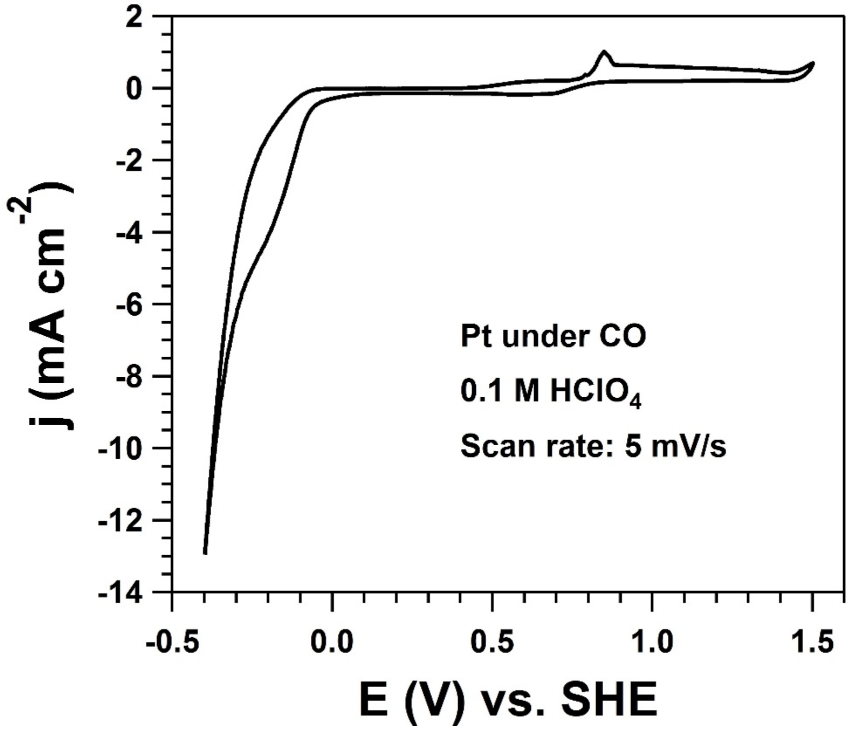

Fig. S3 Cyclic voltammogram at 5 mV s^{-1} in 0.1 M HClO$_4$ under continuous CO purge corresponding to the spectra in Fig. 3 of the main text.

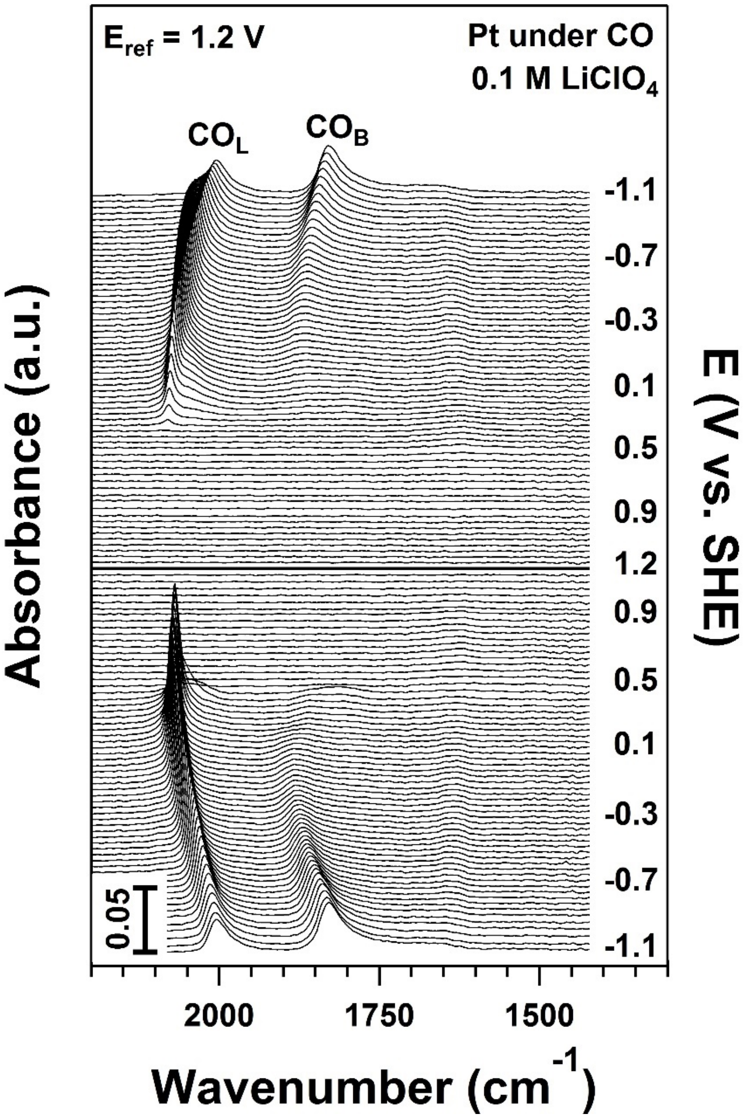

Fig. S4 ATR-SEIRA spectra (4 cm^{-1} resolution, 8 co-added scans) during anodic and cathodic scans from -1.1 V to 1.2 V on chemically deposited Pt film electrode in 0.1 M $LiClO_4$ under continuous CO purge during potential cycling at 5 mV s^{-1}. Reference spectrum collected at 1.2 V. Corresponding CV is presented in Fig. S1.

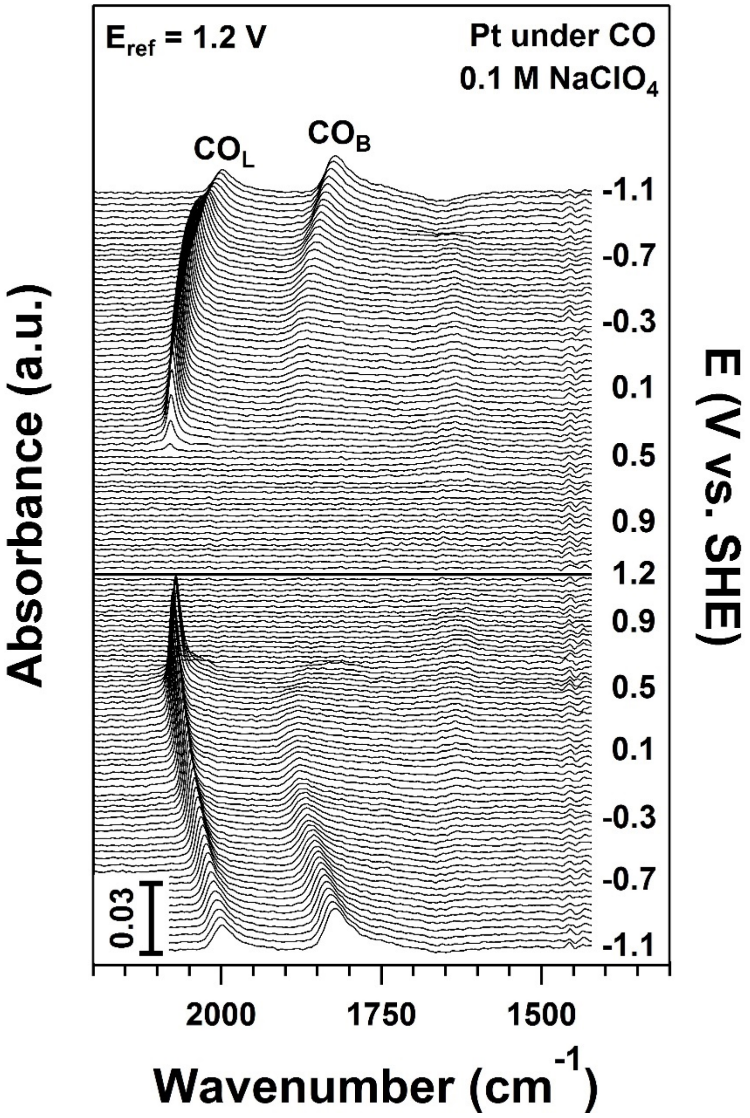

Fig. S5 ATR-SEIRA spectra (4 cm^{-1} resolution, 8 co-added scans) during anodic and cathodic scans from -1.1 V to 1.2 V on chemically deposited Pt film electrode in 0.1 M $NaClO_4$ under continuous CO purge during potential cycling at 5 mV s^{-1}. Reference spectrum collected at 1.2 V. Corresponding CV is presented in Fig. S1.

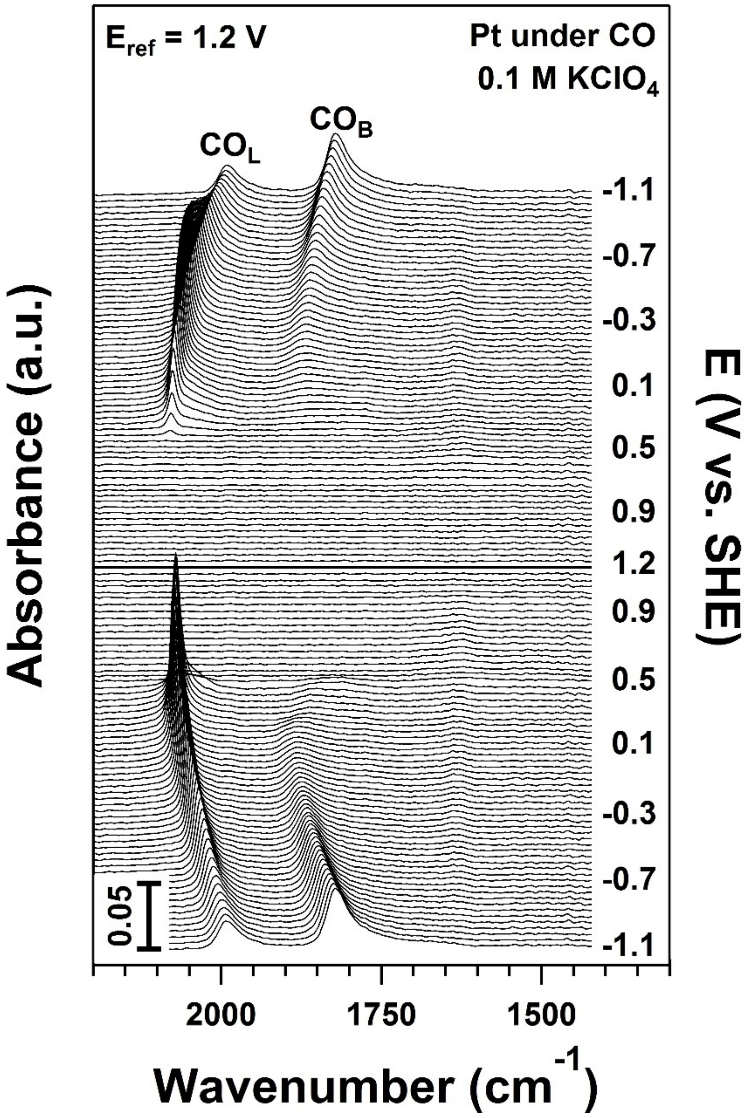

Fig. S6 ATR-SEIRA spectra (4 cm^{-1} resolution, 8 co-added scans) during anodic and cathodic scans from -1.1 V to 1.2 V on chemically deposited Pt film electrode in 0.1 M $KClO_4$ under continuous CO purge during potential cycling at 5 mV s^{-1}. Reference spectrum collected at 1.2 V. Corresponding CV is presented in Fig. S1.

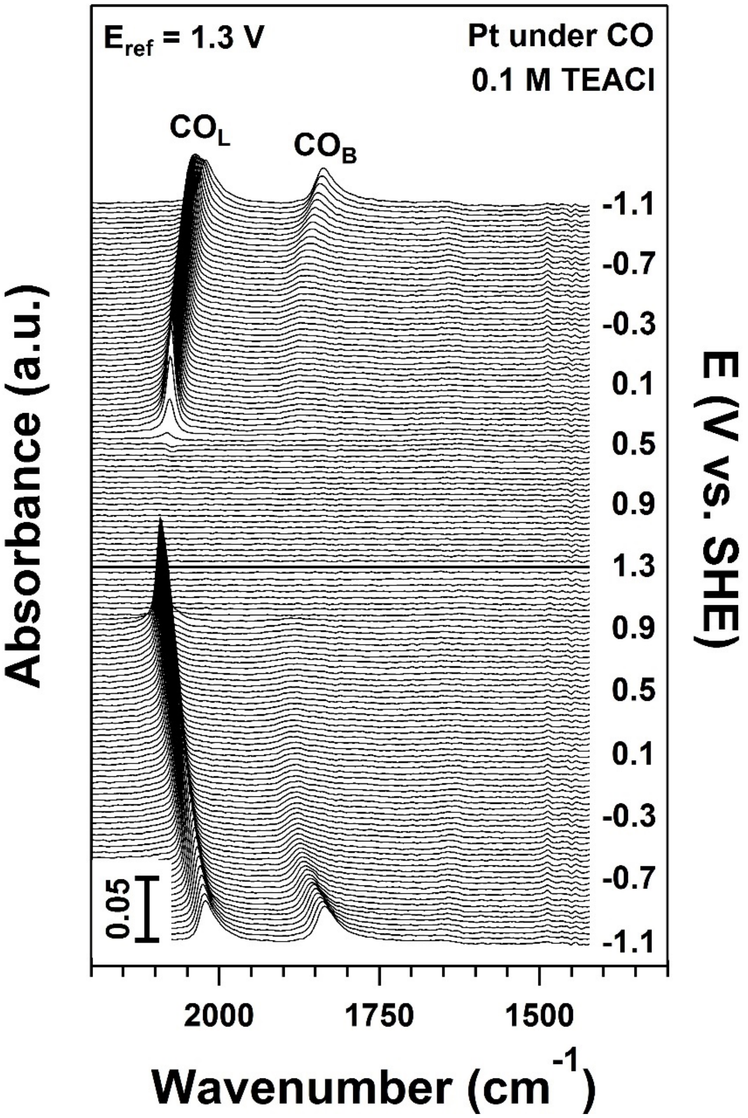

Fig. S7 ATR-SEIRA spectra (4 cm^{-1} resolution, 8 co-added scans) during anodic and cathodic scans from -1.1 V to 1.3 V on chemically deposited Pt film electrode in 0.1 M TEACl under continuous CO purge during potential cycling at 5 mV s^{-1}. Reference spectrum collected at 1.3 V. Corresponding CV is presented in Fig. S1.

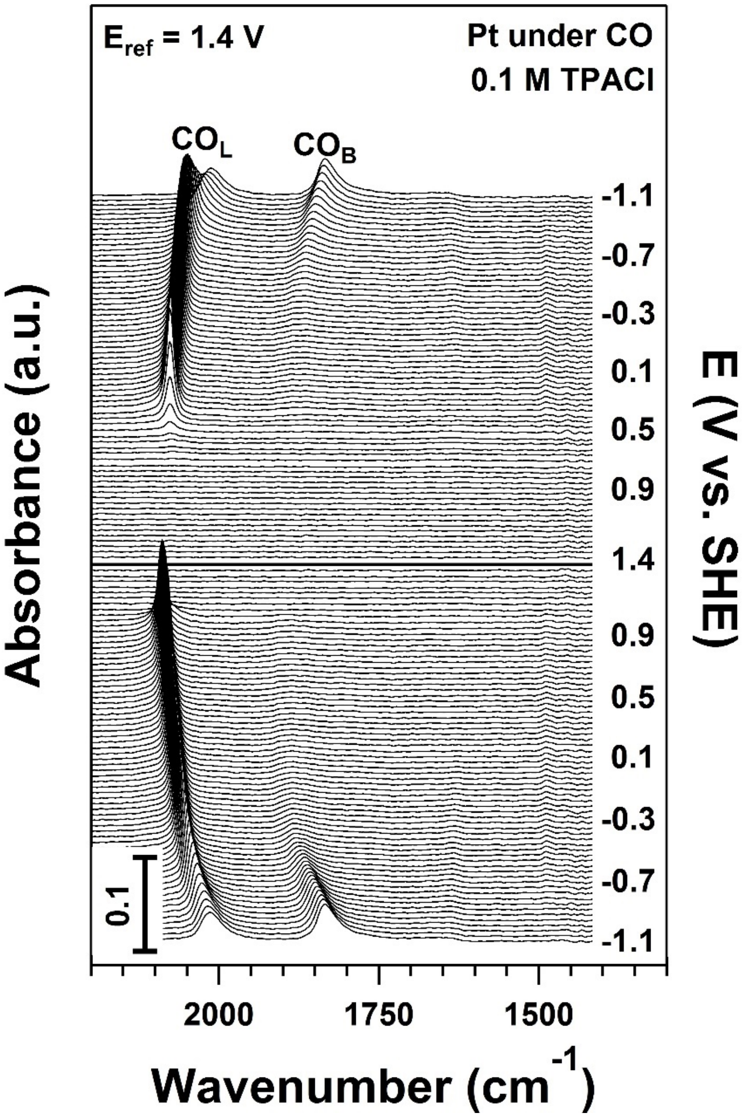

Fig. S8 ATR-SEIRA spectra (4 cm^{-1} resolution, 8 co-added scans) during anodic and cathodic scans from -1.1 V to 1.4 V on chemically deposited Pt film electrode in 0.1 M TPACl under continuous CO purge during potential cycling at 5 mV s^{-1}. Reference spectrum collected at 1.4 V. Corresponding CV is presented in Fig. S1.

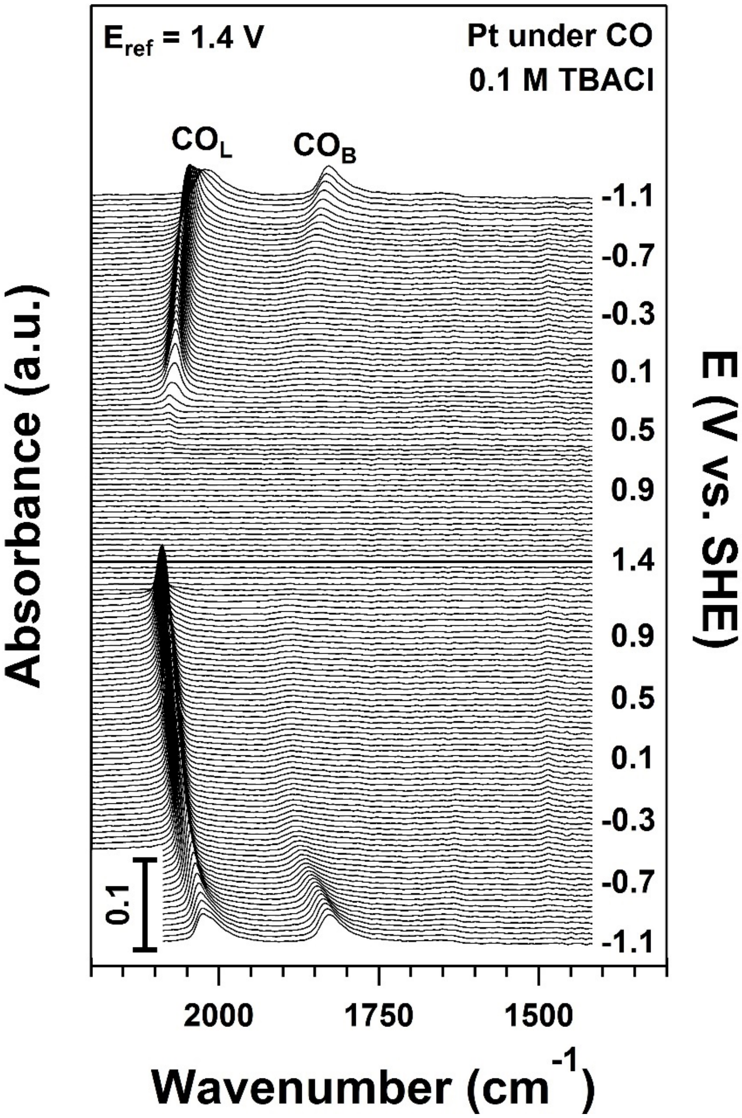

Fig. S9 ATR-SEIRA spectra (4 cm^{-1} resolution, 8 co-added scans) during anodic and cathodic scans from -1.1 V to 1.4 V on chemically deposited Pt film electrode in 0.1 M TBACl under continuous CO purge during potential cycling at 5 mV s^{-1}. Reference spectrum collected at 1.4 V. Corresponding CV is presented in Fig. S1.

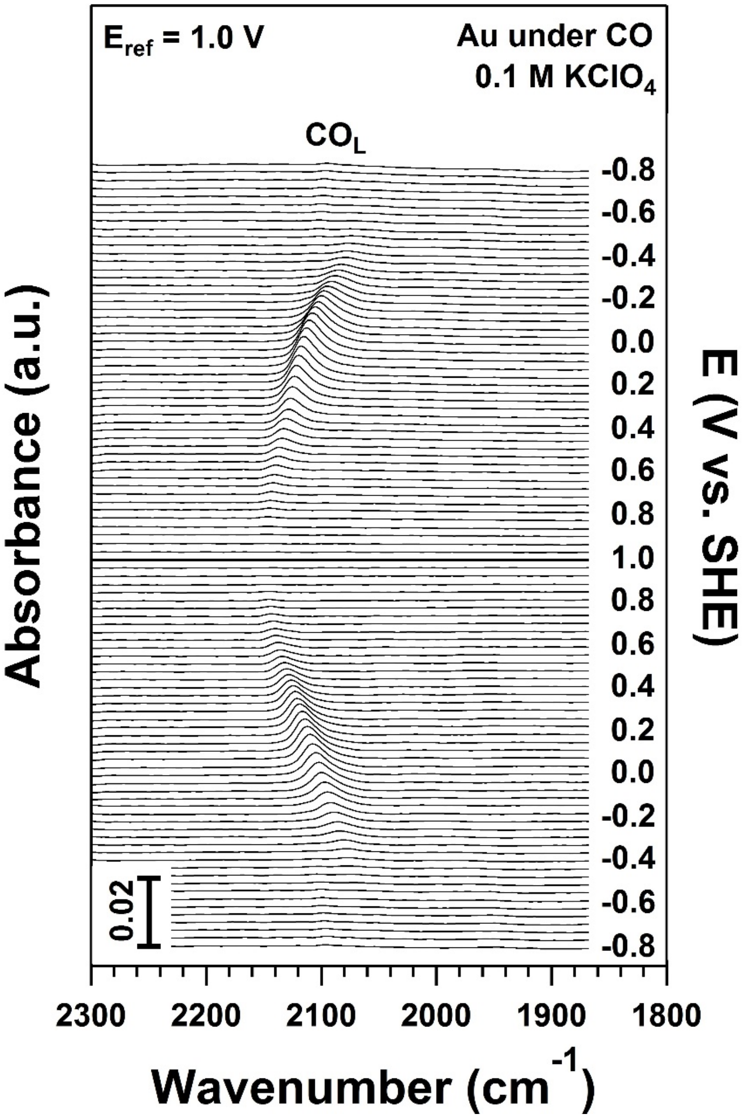

Fig. S10 ATR-SEIRA spectra (4 cm^{-1} resolution, 8 co-added scans) during anodic and cathodic scans at 5 mV s-1 from -0.8 V to 1.0 V vs. SHE on chemically deposited Au film electrode in 0.1 M $KClO_4$ under continuous CO purge. Reference spectrum collected at 1.0 V.

References

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2. A. Miki, S. Ye, T. Senzaki and M. Osawa, *Journal of Electroanalytical Chemistry*, 2004, **563**, 23-31.
3. S. Karmalkar and J. Banerjee, *Journal of The Electrochemical Society*, 1999, **146**, 580-584.
4. M. Dunwell, Y. Yan and B. Xu, *Surface Science*, 2015, DOI: http://dx.doi.org/10.1016/j.susc.2015.12.019.