

Supporting Information

Reconstructed PbCO₃ with abundant oxygen vacancies for efficient CO₂-to-formate electrocatalysis

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Materials: All chemicals are analytical grade and used without any further purification. Lead acetate ($\text{Pb}(\text{CH}_3\text{COO})_2$, 99%) and lead carbonate (PbCO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1, 2-Epoxypropane (99.5%) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Standard Basic lead carbonate ($\text{Pb}_2(\text{CH}_3\text{COO})_2(\text{OH})_2$, 99%) and Pb powder (Lead, 99.95% metals basis) was purchased from Shanghai Macklin Biochemical Co., Ltd. Anhydrous ethanol (EtOH, 99.7%) was bought from Shanghai Titan Scientific Co., Ltd. Nafion solution (5 wt.%) was bought from Sigma-Aldrich. Potassium hydroxide (KOH, 85%) was bought from Yonghua Chemical Co., Ltd. High purity hydrogen (H_2 , 99.999%), argon (Ar, 99.9%) and carbon dioxide (CO_2 , 99.99%) gases were provided by Shanghai Jiajie Gas Co., Ltd. Deionized (DI) water ($>18.25 \text{ M}\Omega \text{ cm}$) used in all experiments was supplied by Millipore System (Millipore, Billerica, MA).

Synthesis of $\text{Pb}_2(\text{CH}_3\text{COO})_2(\text{OH})_2$ precatalyst: The $\text{Pb}_2(\text{CH}_3\text{COO})_2(\text{OH})_2$ precatalyst was synthesized through a wet chemical method. In a typical synthesis procedure, 1 mmol $\text{Pb}(\text{CH}_3\text{COO})_2$ was dissolved into 1 mL deionized water to obtain a transparent solution. The solution was then added to 4 mL ethanol with stirring in a vial. Then, 2 mL 1, 2-epoxypropane was quickly added to the vial followed with vigorous stirring for 1 min. The $\text{Pb}_2(\text{CH}_3\text{COO})_2(\text{OH})_2$ precatalyst was then obtained through centrifugation after 6 h. After dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ overnight, the $\text{Pb}_2(\text{CH}_3\text{COO})_2(\text{OH})_2$ precatalyst was directly used as electrocatalyst.

Characterizations: The morphologies of all samples were analyzed by scanning electron microscopy (SEM, Hitachi S4800). The corresponding crystal structure was characterized by X-ray diffraction (XRD, D/max2550V). Scanning transmission electron microscopy (STEM) and transmission electron microscope (TEM) characterization was performed using ThermoFisher Talos F200X. High angle annular dark field (HAADF-STEM) images were recorded using a convergence semi angle of 11 mrad, and inner- and outer collection angles of 59 and 200 mrad, respectively. Energy dispersive X-ray spectroscopy (EDS) was carried out using 4 in-column Super-X detectors. The chemical states of the elements were examined by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD), and the energy corrections were calibrated by referencing the C 1s peak of adventitious carbon to 284.8 eV.

XAFS measurements at Pb L₃-edge in transmission mode were performed at the BL14W1 in Shanghai Synchrotron Radiation Facility. The electron beam energy was 3.5 GeV and the stored current was 230 mA (top-up). A 38-pole wiggler with the maximum magnetic field of 1.2 T inserted in the straight section of the storage ring was used. XAFS data were collected using a double-crystal Si (111) monochromator. The raw data analysis was performed using IFEFFIT software package according to the standard data analysis procedures.

FTIR spectroscopy was characterized on a Nicolet 6700 spectrometer with the spectral range of 3000-1000 cm⁻¹

Electrochemical measurements: All electrochemical measurements were carried out

on a CHI 660E electrochemical station. Ag/AgCl electrode with a saturated KCl filling solution was used as the reference electrode. Potential versus RHE was calculated as $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.205 \text{ V} + 0.0591 \text{ V} \times \text{pH}$. A mass flow controller was used to control the flow rate of CO₂ or Ar to 20 sccm.

CO₂RR was carried in a three-part homemade flow cell. The cell was consisted of a cathode and anode chamber separated by an anion exchange membrane (Fumasep FAB-PK-130). The cathodic chamber was separated from the gas chamber by a 1.5×1.5 cm² gas diffusion electrode (GDE). A plastic plate with a 0.7×0.7 cm² window was placed between the GDE and cathode chamber. Silicone gaskets were placed in between different chambers for sealing. For making GDE, a certain amount of ink was sprayed on gas diffusion layer (GDL, Sigracet 28 BC) using an air brush, the loading amount of catalyst was 1 mg cm⁻². A treated nickel foam (2.5×2.5 cm²) was used as counter electrode. 30 mL of 1.0 M KOH electrolyte was used as catholyte and anolyte, respectively. The flow rate of CO₂ was set to 20 sccm; the flow rate of the electrolyte was kept at 10.02 mL min⁻¹ in two chambers. Gas-phase products of CO₂ reduction were quantified by a gas chromatography (GC 2060). The liquid products were quantified using ¹H nuclear magnetic resonance (NMR, Varian 700MHz spectrometer), in which 500 μL of the electrolyte was mixed with 100 μL of D₂O (with TMSP as the internal standard). The data processing of the NMR spectra was performed using the Bruker software Topspin. The electrochemical impedance spectroscopy (EIS) measurement was conducted by applying at -0.5 V (vs. RHE) with an amplitude of 5 mV in a frequency range from 10⁵ Hz to 0.01 Hz.

Density Functional Theory (DFT) calculations: All of the DFT calculations were performed with the generalized gradient approximation (GGA) functional of the Perdew-Burke-Ernzerhof (PBE) ¹ using Vienna Ab-initio Simulation Package (VASP) software. ^{2, 3} The project-augmented wave (PAW) was used to describe the interaction between the atomic nucleus and electron⁴. Bader charge analysis was used to determine the atomic charge⁵. The valence electronic states were expanded in plane wave basis sets with an energy cutoff at 450 eV. DFT-D3(BJ) is used to correct Van der Waals force in our system^{6, 7}. The Broyden method was employed for geometric relaxation until the maximal force on each relaxed atom was less than 0.05 eV/Å. PbCO₃ (001) surface was modeled with three layers with a vacuum of 15 Å. During optimization, the bottom one layers of the slab were fixed, and the top two layers were fully relaxed. A p(3×2) PbCO₃ (001) surface slab with a corresponding 2×2×1 k-point mesh was used. The constrained optimization method was used to search the transition state, which has been widely verified^{8, 9}.

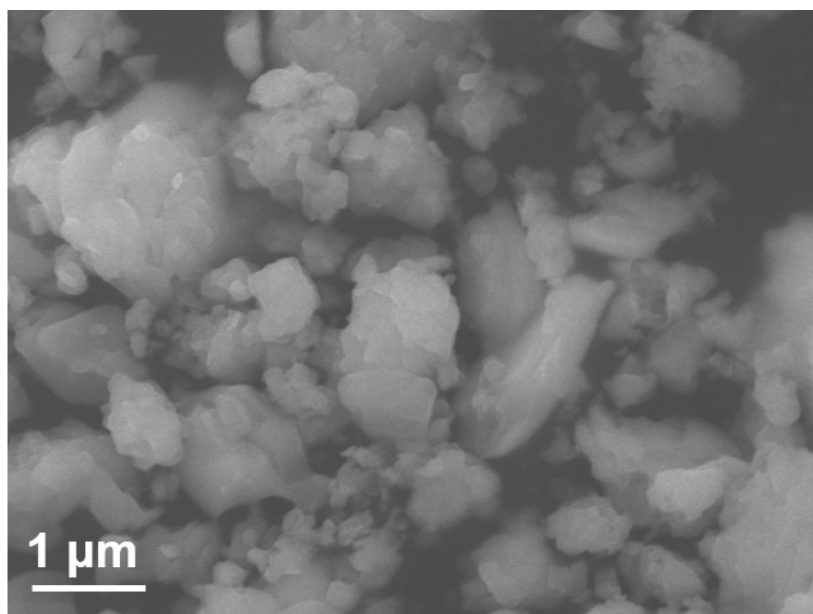


Fig. S1. SEM image of the $\text{Pb}_2(\text{CH}_3\text{COO})_2(\text{OH})_2$ pre-catalyst before electroreduction.

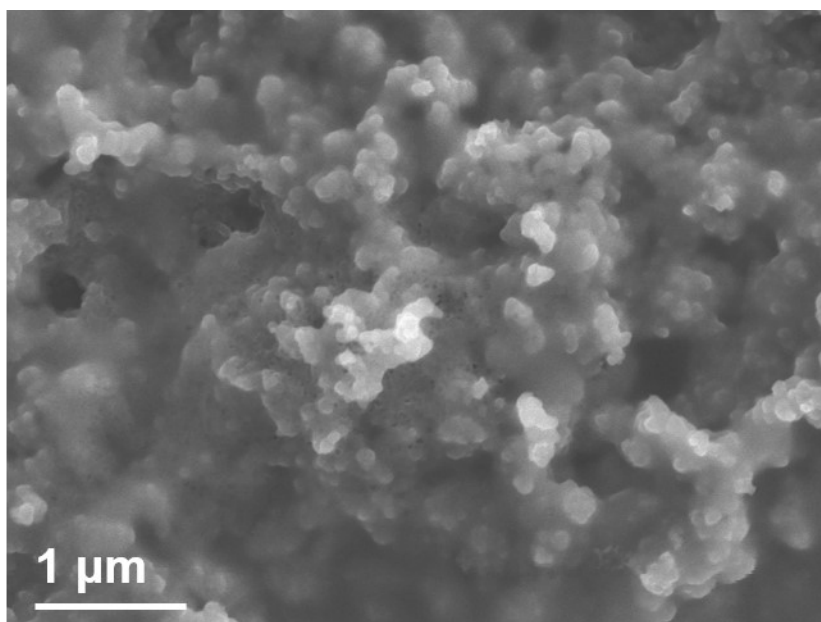


Fig. S2. SEM image of the O-PbCO₃ electrocatalyst after electroreduction.

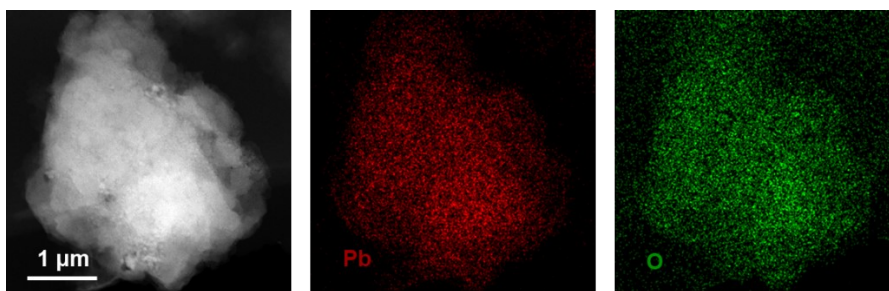


Fig. S3. HAADF and corresponding EDS mapping images of the $\text{Pb}_2(\text{CH}_3\text{COO})_2(\text{OH})_2$ precatalyst before electroreduction.

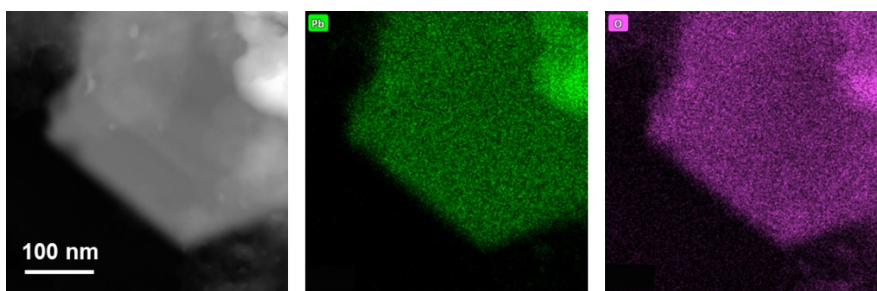


Fig. S4. HAADF and corresponding EDS mapping images of the O-PbCO₃ electrocatalyst after electroreduction.

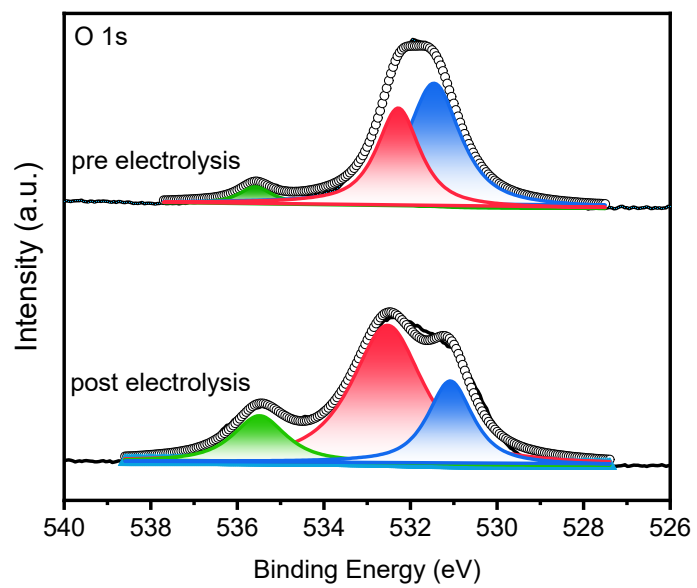


Fig. S5. O 1s XPS spectra of $\text{Pb}_2(\text{OH})_2(\text{CH}_3\text{COO})_2$ (up) and O-PbCO_3 (down).

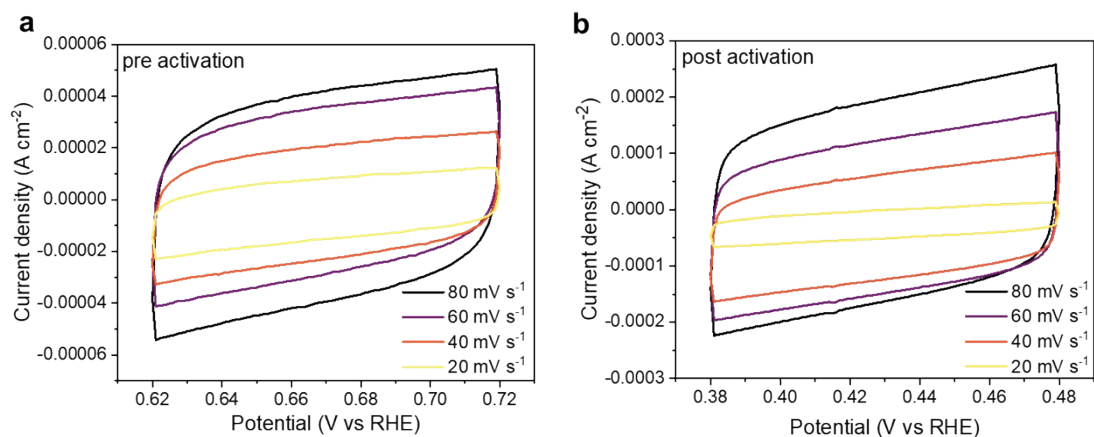


Fig. S6. Cyclic voltammograms with various scan rates for (a) $\text{Pb}_2(\text{OH})_2(\text{CH}_3\text{COO})_2$ precatalyst and (b) O-PbCO_3 after electrolysis in 1.0 M KOH under a current density of 100 mA cm^{-2} for 1 h.

Notes: CVs measurements were carried out at a non-Faradaic potential range. The scan rates were 20 to 80 mV s^{-1} . The double-layer capacitance (C_{dl}) was estimated by plotting the $\Delta j/2 = (j_a - j_c)/2$ at 0.67 V and 0.43V vs. RHE against the scan rate for $\text{Pb}_2(\text{OH})_2(\text{CH}_3\text{COO})_2$ precatalyst and O-PbCO_3 respectively.

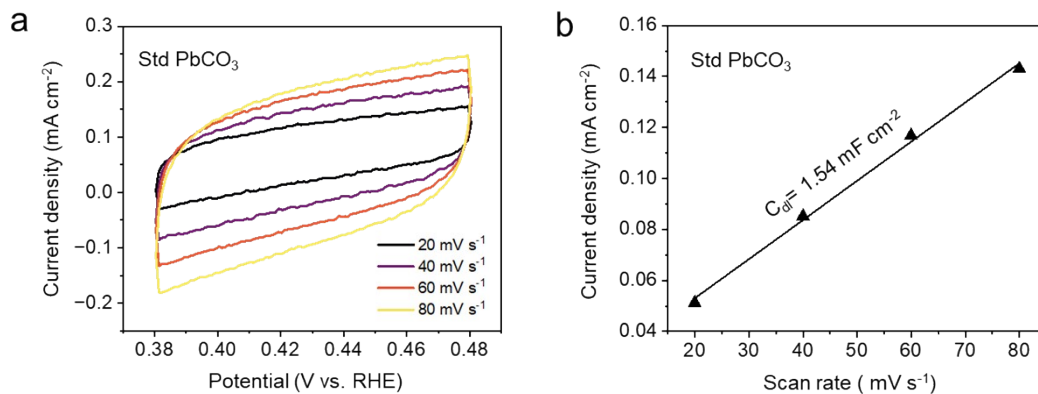


Fig. S7. (a) Cyclic voltammograms with various scan rates for Std PbCO₃ and (b) current density due to double-layer charging plotted against cyclic voltammetry scan rate for Std PbCO₃.

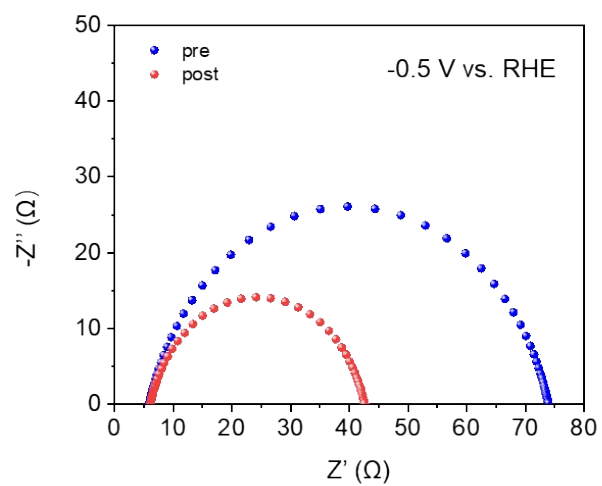


Fig. S8. Nyquist plots of $\text{Pb}_2(\text{OH})_2(\text{CH}_3\text{COO})_2$ and O-PbCO_3 in 1.0 M KOH aqueous solution at -0.5 V (vs. RHE; non-iR corrected), showing the faster electron transfer for the O-PbCO_3 than that of precatalyst $\text{Pb}_2(\text{OH})_2(\text{CH}_3\text{COO})_2$.

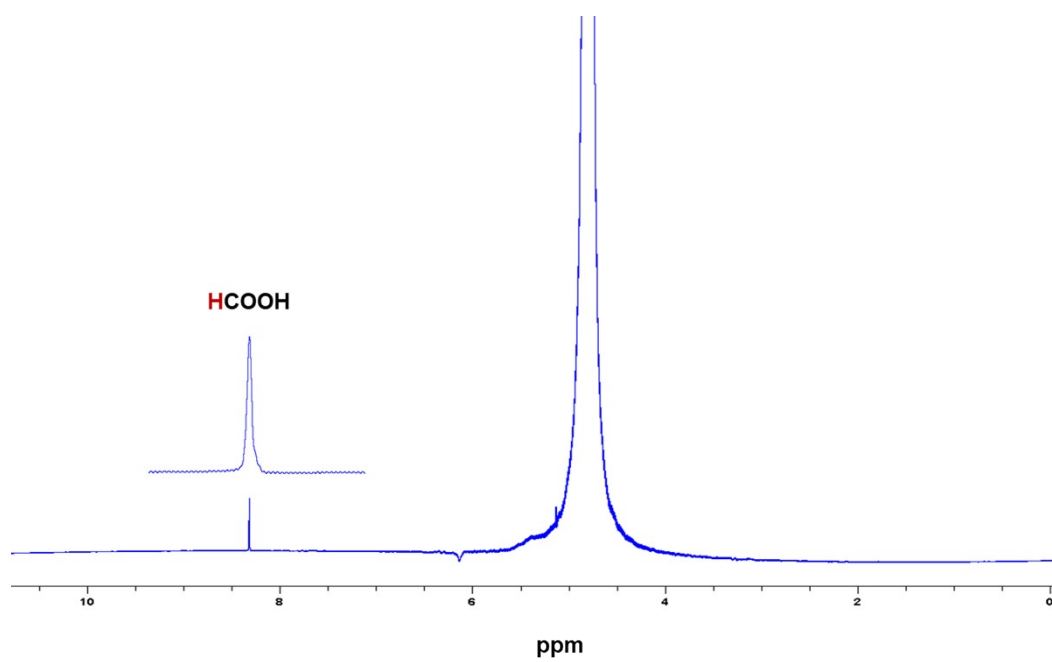


Fig. S9. Representative $^1\text{H-NMR}$ spectrum obtained from the catholyte of CO_2 reduction in a flow cell. DMSO (Dimethyl sulphoxide) is used as an internal standard for quantification of liquid products.

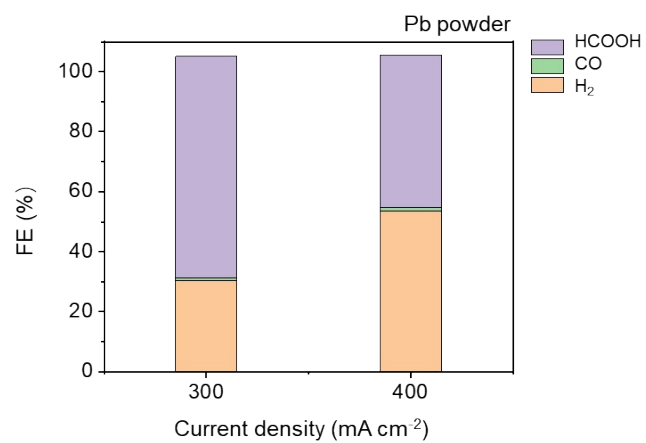


Fig. S10. Current density-dependent FEs of Pb powder under 300 and 400 mA cm⁻².

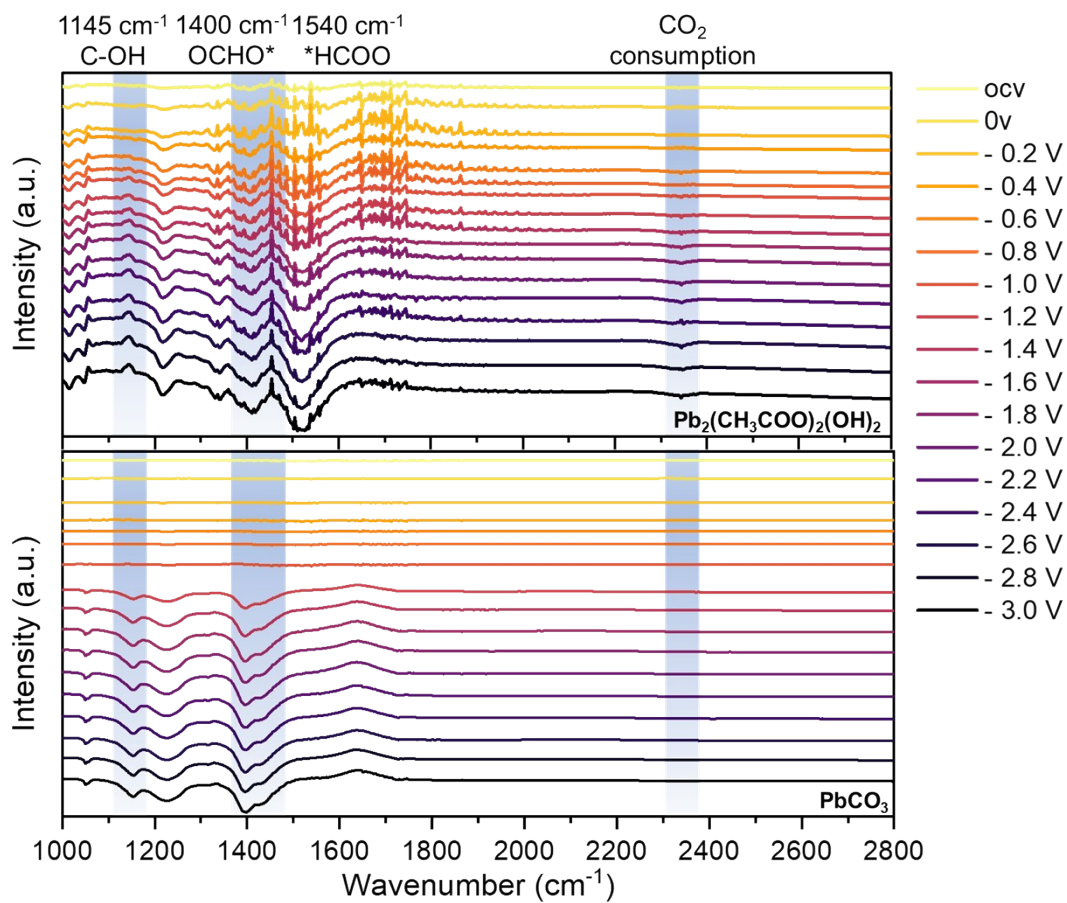


Fig. S11. Potential-dependent SEIRAS spectra of standard PbCO₃ control and O-PbCO₃ catalyst.

Reference

1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865-3868.
2. G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, 47, 558-561.
3. G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, 49, 14251-14269.
4. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, 46, 6671-6687.
5. W. Tang, E. Sanville and G. Henkelman, *J. Phys.: Condens.Matter*, 2009, 21, 084204.
6. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, 32, 1456-1465.
7. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, 132, 154104.
8. A. Michaelides, Z. P. Liu, C. J. Zhang, A. Alavi, D. A. King and P. Hu, *J. Am. Chem. Soc.*, 2003, 125, 3704-3705.
9. J. F. Chen, M. L. Jia, P. J. Hu and H. F. Wang, *J. Comput. Chem.*, 2021, 42, 379-391.