Electronic Supplementary Information

Surface coverage control for dramatic enhancement of thermal CO oxidation by precise potential tuning of metal supported catalysts

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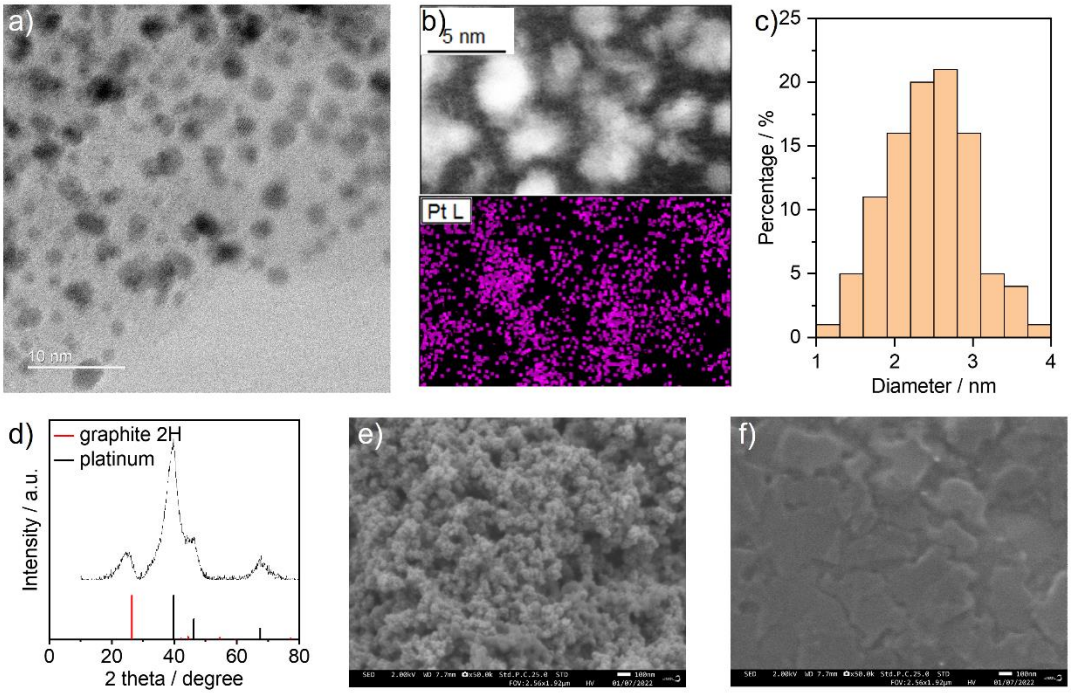

Fig. S1. a) TEM image, **b)** EDX-mapping image, **c)** distribution of particle sizes, **d)** XRD characterization of pristine Pt/C catalyst and SEM images of **e)** pristine Pt/C layer on CP substrate and **f)** pristine CP substrate.

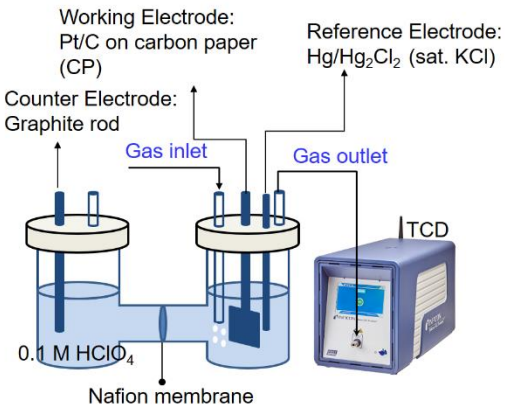

Fig. S2. Schematic representation of the two-compartment cell (H-cell) used for catalytic measurement.

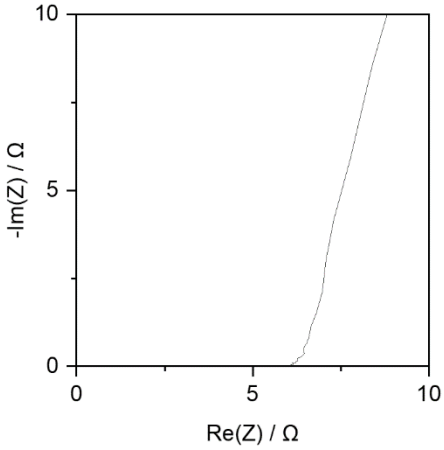

Fig. S3. PEIS profile for resistance determination. Conditions: WE: 3 mg Pt/C on 2×2 cm^2 CP; potential: 0.70 V vs. RHE; initial frequency: 200 kHz; final frequency: 100 mHz; gas flow rate: 20 ml min^{-1}; pressure: 101 kPa; p(CO): 25 kPa; $p(O_2)$: 10 kPa; balance: Ar; RE: Hg/Hg_2Cl_2 (sat. KCl); CE: graphite rod; 295 K; stirring rate: 750 rpm; 0.1 M $HClO_4$.

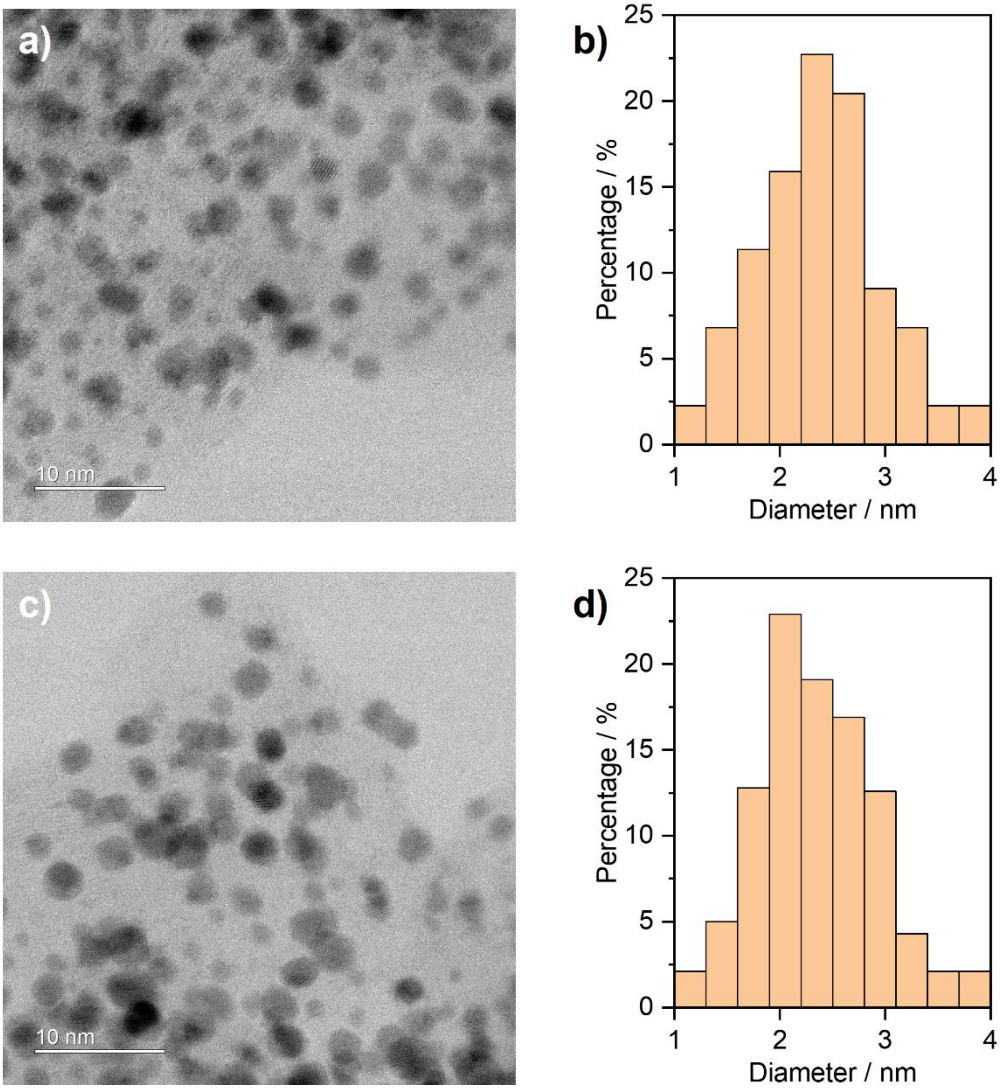

Fig. S4. a) TEM image and **b)** distribution of particle sizes of Pt/C catalyst after OCP-shift measurement. **c)** TEM image and **d)** distribution of particle sizes of Pt/C catalyst after 4-h reaction under 25 kPa CO and 10 kPa O_2 with 0.70 V vs. RHE applied.

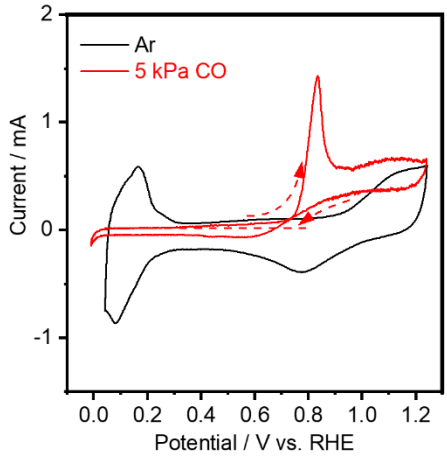

Fig. S5. Cyclic voltammetry (CV) characterization of Pt/C catalyst under pure Ar or diluted CO. Conditions: WE: 0.75 mg Pt/C on 1×1 cm^2 CP; gas flow rate: 20 ml min^{-1}; pressure: 101 kPa; Scan rate: 2 mV s^{-1}; RE: Hg/Hg_2Cl_2 (sat. KCl); CE: graphite rod; 295 K; stirring rate: 750 rpm; 0.1 M $HClO_4$.

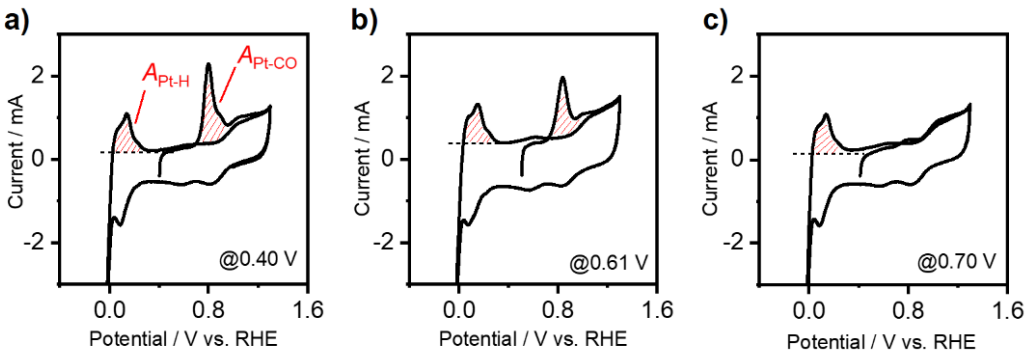

Fig. S6. CV profiles used for CO* coverage (θ_{CO}) calculation at **a)** 0.40 V, **b)** 0.61 V, and **c)** 0.70 V vs. RHE. WE: 0.75 mg Pt/C on 1×1 cm^2 CP; gas flow rate: 20 ml min^{-1}; pressure: 101 kPa; Scan rate: 1 mV s^{-1}; RE: Hg/Hg_2Cl_2 (sat. KCl); CE: graphite rod; 295 K; stirring rate: 750 rpm; 0.1 M $HClO_4$.

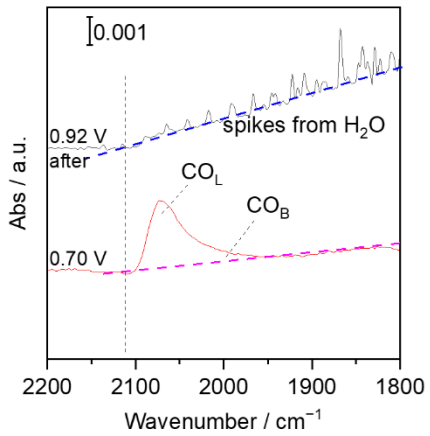

Fig. S7. Infrared spectra at 0.70 V (red) and 0.92 V (black) vs. RHE under 25 kPa CO and 10 kPa O_2. The baseline for the integral of CO* band was determined based on the baseline appearing in the case of 0.92 V.

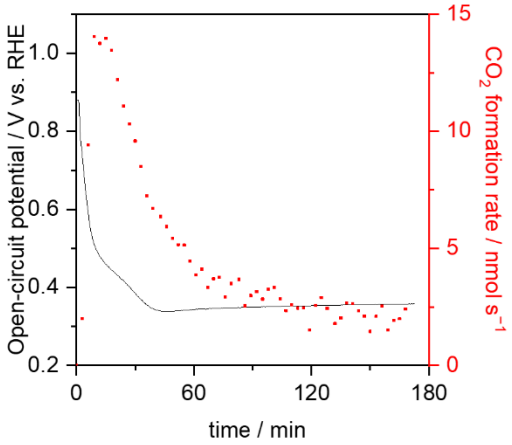

Fig. S8. Time evolution of open-circuit potential of Pt/C catalyst during CO oxidation and corresponding reaction rate. Conditions: WE: 3 mg Pt/C on 2×2 cm^2 CP; gas flow rate: 20 ml min^{-1}; pressure: 101 kPa; p(CO): 25 kPa; $p(O_2)$: 10 kPa; RE: Hg/Hg_2Cl_2 (sat. KCl); CE: graphite rod; stirring rate: 750 rpm; 295 K; 0.1 M $HClO_4$.

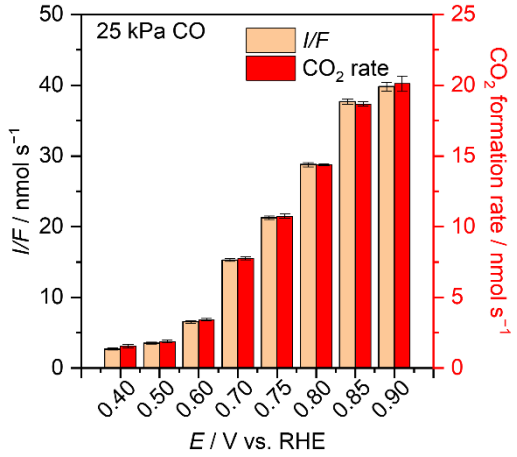

Fig. S9. Comparison of electric current and corresponding CO_2 formation rate in unit of nmol s^{-1} at varied potentials, showing a ratio of ~2 and indicating a FE of ~100% for electrochemical CO oxidation under the given condition. Conditions: WE: 3 mg Pt/C on 2×2 cm^2 CP; gas flow rate: 20 ml min^{-1}; pressure: 101 kPa; p(CO): 25 kPa; balance: Ar; RE: Hg/Hg_2Cl_2 (sat. KCl); CE: graphite rod; 295 K; stirring rate: 750 rpm; 0.1 M $HClO_4$.

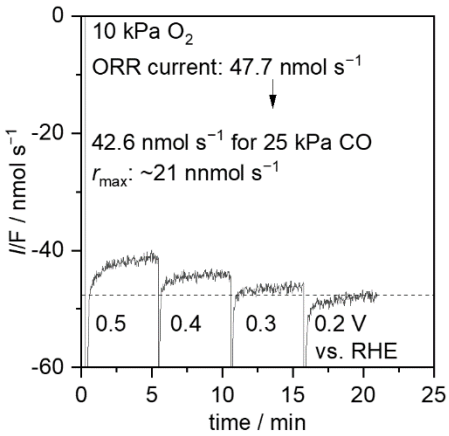

Fig. S10. Measurement of diffusion-limited ORR current for the estimation of diffusion-limited CO oxidation rate. Conditions: WE: 3 mg Pt/C on 2×2 cm^2 CP; gas flow rate: 20 ml min^{-1}; pressure: 101 kPa; $p(O_2)$: 10 kPa; balance: Ar; RE: Hg/Hg_2Cl_2 (sat. KCl); CE: graphite rod; 295 K; stirring rate: 750 rpm; 0.1 M $HClO_4$.

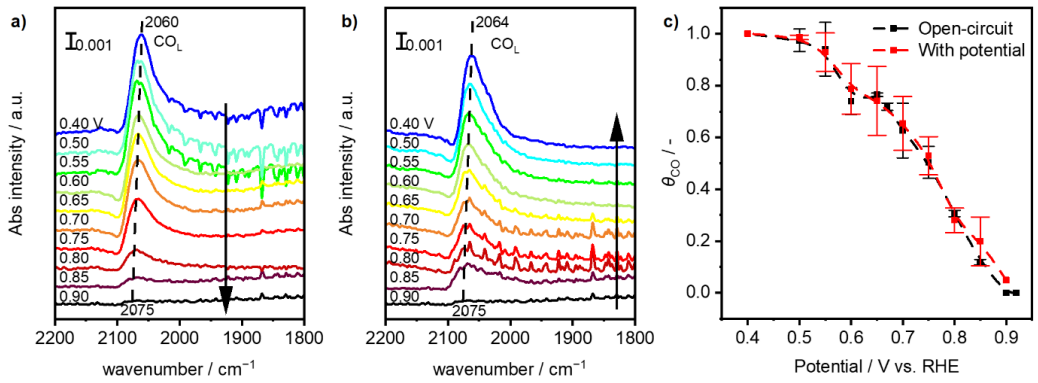

Fig. S11. The evolution of infrared spectra with external potential **a)** changing from 0.40 V to 0.90 V vs. RHE and **b)** changing from 0.90 V back to 0.40 V vs. RHE. **c)** Calculated θ_{CO} as a function of external potential based on ATR-IRAS. Conditions: WE: Pt/C on IRE; gas flow rate: 20 ml min^{-1}; pressure: 101 kPa; balance: Ar; RE: Hg/Hg_2Cl_2 (sat. KCl); CE: Pt wire; 0.1 M $HClO_4$; 295 K.

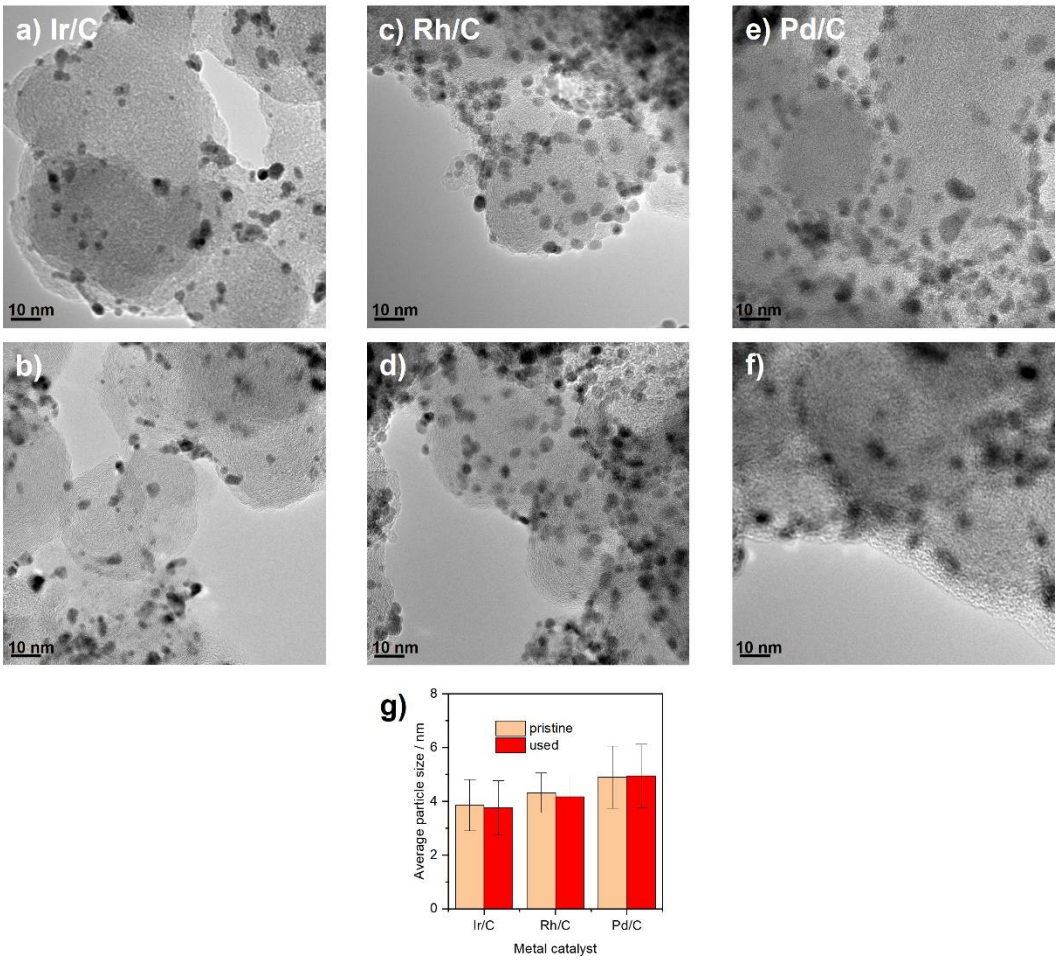

Fig. S12.TEM images of **a)** pristine Ir/C, **b)** used Ir/C, **c)** pristine Rh/C, **d)** used Rh/C, **e)** pristine Pd/C and **f)** used Pd/C, and **g)** statistical comparison of particle sizes of pristine and used catalysts. Reaction potential: 0.75 V vs. RHE for Ir/C, 0.70 V for Rh/C and 0.90 V for Pd/C (potentials for the best FE).

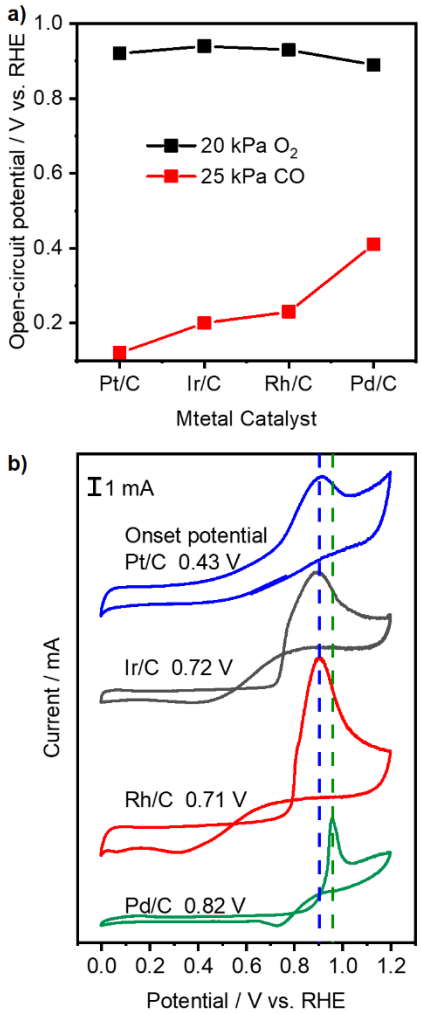

Fig. S13. a) OCP values of metal catalysts under 20 kPa O_2 or 25 kPa CO. **b)** CV profiles of metal catalysts under 25 kPa CO. Conditions: WE: 3 mg metal/C on 2×2 cm^2 CP; gas flow rate: 20 ml min^{-1}; pressure: 101 kPa; balance: Ar; RE: Hg/Hg_2Cl_2 (sat. KCl); CE: graphite rod; stirring rate: 750 rpm; scan rate: 2 mV s^{-1}; 295 K; 0.1 M $HClO_4$.

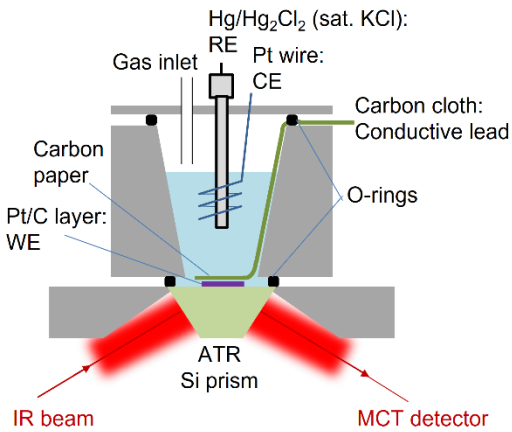

Fig. S14. Schematic presentation of the electrochemical cell for in situ attenuated total reflection-infrared absorption spectroscopy (ATR-IRAS) measurement.