Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Surface Electrochemistry of CO_2 Reduction and CO Oxidation on Sm-doped CeO_{2-x}: Coupling between Ce^{3+} and Carbonate Adsorbates

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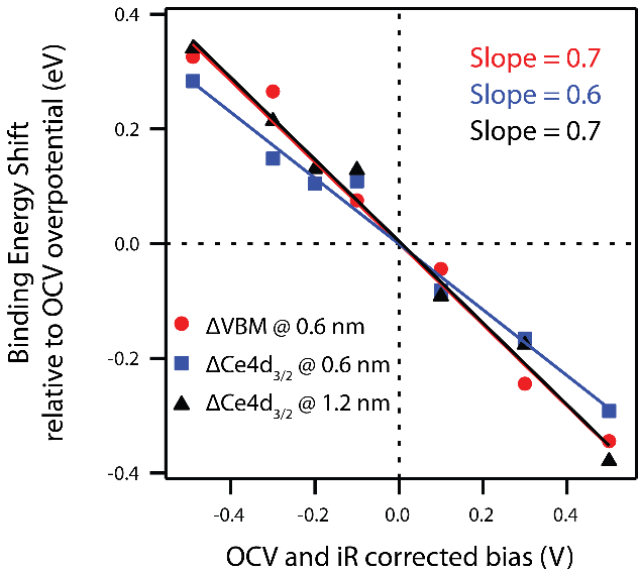

Fig. S1 Binding energy shifts of the valence-band maximum and Ce $4d_{3/2}$ core level peak. The valence-band spectra were taken using 250 eV photon energy with information depth ~0.6 nm. The Ce 4d core level spectra were taken using 370 eV and 790 eV photon energy, with information depths ~ 0.6 nm and 1.2 nm, respectively.

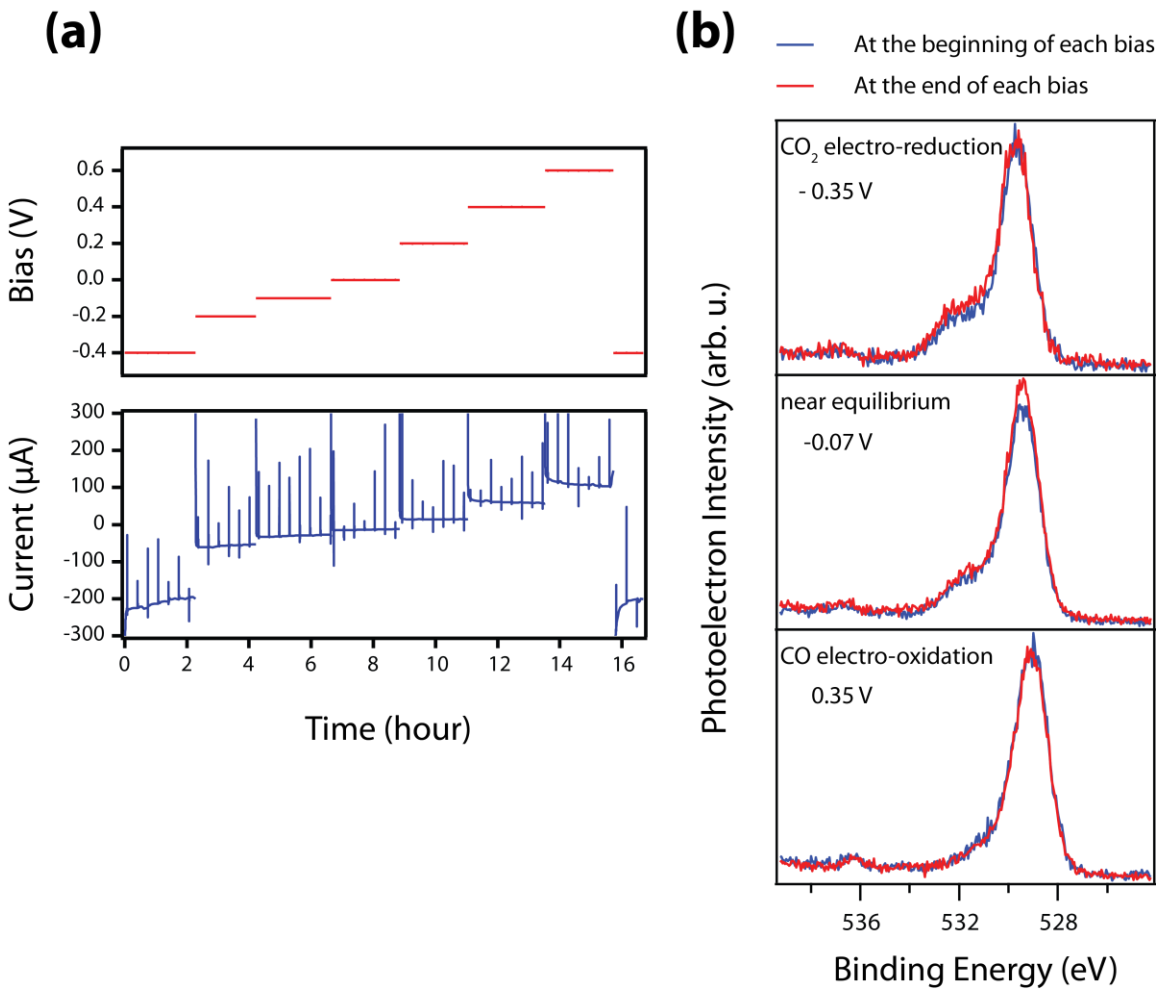

Fig. S2 XPS measurements were made under steady state conditions. (a) The top panel shows the biasing sequence in the experiment. The bottom panel shows the corresponding cell current. The spikes in the current curves are due to the electrochemical impedance spectroscopy measurement. The last bias point was to repeat the initial measurement, in order to confirm the observations were reproducible. (b) The O 1s spectra taken at 790 eV photon energy at the beginning and end of three typical biasing conditions. The excellent alignment of these spectra substantiates that the system was at steady state.

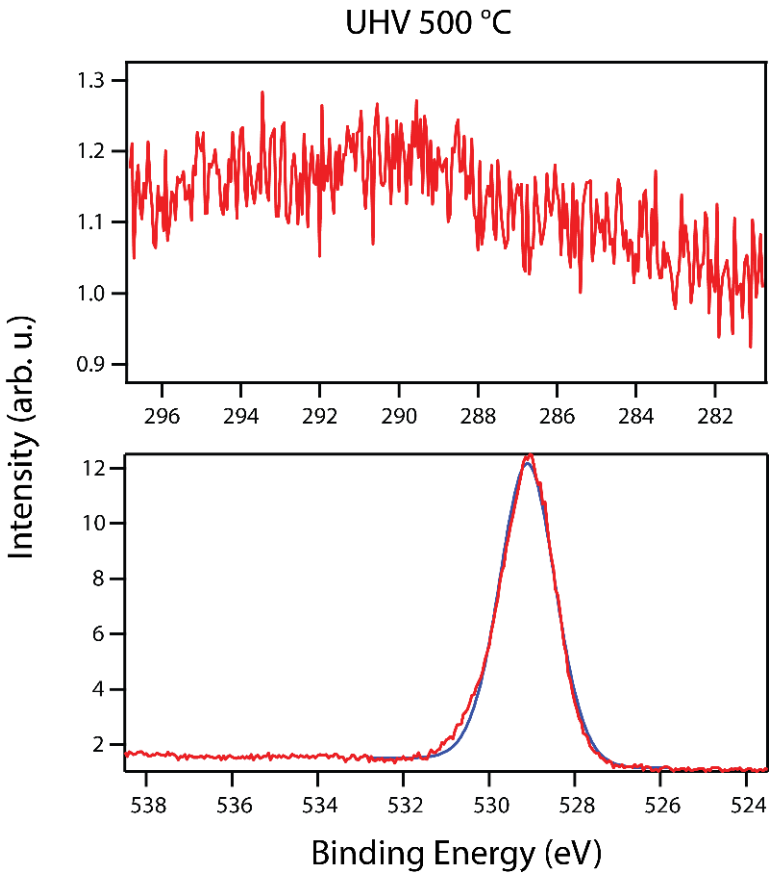

Fig. S3 The C1s (top) and O1s (bottom) photoemission spectra at 500 ˚C and 3×10^{-8} Torr high vacuum. In the C1s spectra (taken with 490 eV photon energy), no significant photoemission peak was detected. In the O1s spectra (taken with 609 eV photon energy), the symmetric blue peak is attributed to the lattice oxygen while the small shoulder to the left is due to the segregated silicon impurity. Neither carbon nor sulfur were observed under such conditions.

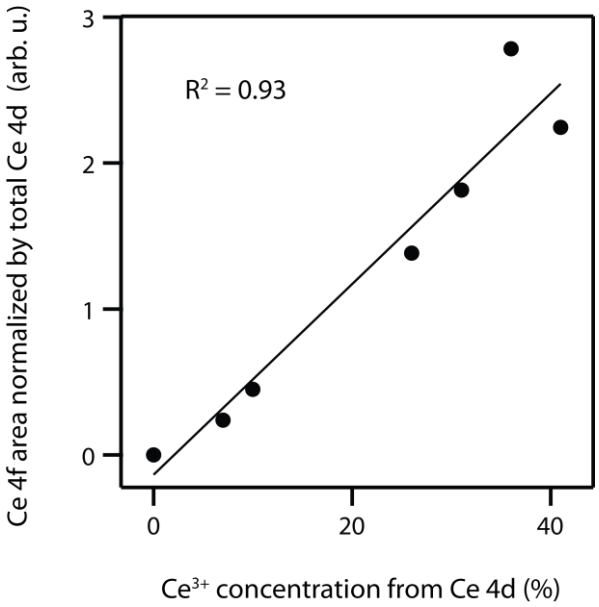

Fig. S4 Linear correlation between the Ce 4f intensity (normalized by the total Ce 4d intensity) and the Ce^{3+} concentration determined from Ce 4d core level spectra. The slope is 6.5.