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1. Experimental Procedures

1.1 Electrocatalyst preparation

A series of carbon-supported palladium catalysts were prepared via wet impregnation using Pd acetylacetonate ($\text{Pd}(\text{acac})_2$, Aldrich, 0.096 mmol, 99%) as the palladium precursor.^[1] The precursor was dissolved in 2.7 mL of acetone (Aldrich, extra dry sealed under nitrogen) and added dropwise to 1 g of carbon black (Cabot, Vulcan XC72R) while stirring continuously, resulting in a final metal loading of 1 wt%. The mixture was continuously stirred for 2 h at room temperature, then dried for 16 h at 40 °C under nitrogen flow. Catalysts with different nominal Pd loadings (1, 2, and 4 wt%) were prepared by adjusting the amount of the carbon support used in the impregnation step, denoted as $\text{Pd}_x\text{Ac}/\text{C}$ ($\text{Pd}_1\text{Ac}/\text{C}$, $\text{Pd}_2\text{Ac}/\text{C}$, and $\text{Pd}_4\text{Ac}/\text{C}$ for loading amounts 1, 2, and 4 wt% respectively).

As a reference, a high-loading (63 wt%) Pd nanoparticle sample was produced via electrodeposition.^[2] A glassy carbon electrode modified with a $81.5 \mu\text{g cm}^{-2}$ thin-film of carbon black was immersed in an electrochemical cell containing a 0.1 M aqueous solution of HClO_4 and 1 mM of PdCl_2 . Electrodeposition was performed by applying 5 CVs at 10 mV s^{-1} within the potential range of 1.2 - 0.05 V_{RHE} .

1.2. Preparation of working electrode

To prepare a catalyst ink, 11.9 mg of $\text{Pd}_1\text{Ac}/\text{C}$ was suspended in a 1 mL mixture of Millipore water and isopropanol (4:1 in volume) with 7 μL Nafion solution (Aldrich, 5 wt%). After horn sonification (Branson, Sonic Dismembrator 150I), 20 μL of catalyst ink was deposited onto a

mirror-polished glassy carbon electrode and left to dry at room temperature. The amount of Pd on the working electrode was fixed at $10 \mu\text{g}_{\text{Pd}} \text{cm}^{-2}$.

1.3. Characterization of Pd_xAc/C catalysts

The particle size distribution of Pd atomic clusters supported on the carbon was determined by HAADF-STEM using a probe-corrected ThermoScientific Titan Themis 60-300 operated at 300 kV. ImageJ software (without automated processing of the image) was utilized for the size analysis by measuring over 2000 particles on micrographs taken from three different areas of the TEM grid. The mean cluster diameter was calculated by dividing the sum of all measured particle diameters by the total number of clusters. A STEM image of electrodeposited Pd nanoparticle, Pd_{NPs}/C, was obtained using a JEM2100F (JEOL) microscope operated at 200 kV.

The Pd amount in the catalysts was determined by X-ray fluorescence instrument (XRF, Malvern Panalytical, Epsilon 4) with an Ag anode. X-ray diffraction (XRD) spectra were recorded on a Bruker D2 Phaser 2nd Generation with Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range from 20° to 80° using a background-free silicon sample holder. X-ray photoelectron spectroscopy (XPS) data were acquired with a SPECS instrument using a monochromatic Al K_α line at 1486.74 eV, 12.5 kV anode potential, and 24 mA beam current. Emitted photoelectrons were collected using a 150 mm hemispherical energy analyzer (Phoibos 150, SPECS). The high-resolution spectrum for Pd 3d was measured with a pass energy of 20 eV, 0.1 s dwell time, and 0.05 eV steps. The C 1s signal of carbon was used for binding energy calibration and assigned to 284.7 eV. All XPS spectra were deconvoluted using CasaXPS peak fitting software with Shirley background subtractions.

1.4. Electrochemical measurements

Electrocatalytic properties were assessed in a three-compartment electrochemical glass cell with two potentiostats (Gamry, Interface 1010E), a rotator (PINE Research Instrumentation, Wavevortex), and in 0.1 M HClO₄ at 25 °C. The three-electrode configuration comprised a graphite rod as a counter electrode, a saturated Ag/AgCl (Metrohm) as a reference electrode, and a rotating ring disk electrode (RRDE) tip (PINE Research Instrumentation,

AFE6R2GCPT) as the working electrode. The RRDE tip was composed of a glassy carbon disk (5.5 mm in diameter, 0.238 cm² in geometric area) and a Pt ring (2 mm thickness) embedded in a PEEK tip. All potentials reported in this article were expressed in the reversible hydrogen electrode (RHE) scale. The collection efficiency of the RRDE electrode (39.5%) was determined experimentally by using the reversible [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ system at different rotation rates. A 0.1 M HClO₄ electrolyte was prepared with Millipore water (VWR chemicals, <1.1 μS cm⁻¹) and concentrated HClO₄ (Carloth, 70%). All measurements were performed at least three times to ensure reproducibility. Prior to the oxygen reduction measurements, the Pt ring of the RRDE electrode was electrochemically cleaned using cyclic voltammetry (CV) in 0.1 M HClO₄ electrolyte by sweeping the potential between 0.1 and 1.4 V_{RHE} at a scan rate of 400 mV s⁻¹ in N₂-saturated electrolyte until steady CVs were obtained. The background current was collected by measuring a CV in N₂-saturated electrolyte within the potential range from 0.1 to 0.9 V_{RHE} at a scan rate of 10 mV s⁻¹. After purging with O₂, the ORR polarization curves were recorded with a scan rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm. The ring current was maintained at 1.4 V_{RHE} during the ORR polarization on the disk electrode to further oxidize the as-formed H₂O₂. Selectivity of the catalysts toward H₂O₂ formation and the number of electrons transferred (*n*) at the disk electrode were calculated using ring current (*I*_{ring}), disk current (*I*_{disk}), and collection efficiency (*N*) according to the following equations [Equation 1 and Equation 2]: [3-5]

$$\text{H}_2\text{O}_2 (\%) = 200 \frac{I_{\text{ring}}}{N|I_{\text{disk}}| + I_{\text{ring}}} \quad (1)$$

$$n = \frac{4|I_{\text{disk}}|}{|I_{\text{disk}}| + I_{\text{ring}}/N} \quad (2)$$

For the CO stripping test, the electrolyte is first purged with CO for 7 min. After that, the gas is switched to N₂ for 25 min in order to remove the CO from the electrolyte, leaving only adsorbed CO on the Pd surface. Two cyclic voltammograms were then collected between 0.06 and 1.23 V_{RHE} at a scan rate of 50 mV s⁻¹.

To study the impact of CO on the catalyst, the electrolyte was saturated with CO for 15 minutes while applying 0.2 V_{RHE}, following the initial ORR measurement. Subsequently, residual CO was eliminated by flushing the electrolyte with O₂ for 10 min and the second ORR was carried out within the potential range from 0.1 to 0.5 V_{RHE} at a scan rate of 10 mV s⁻¹.

1.5. In-situ/operando electrochemical (EC) ATR-SEIRAS

The in-situ/operando EC ATR-SEIRAS studies were performed using the Fourier transform infrared spectrometer Vertex 80v (Bruker) with an ATR unit (PIKE Technologies, VeeMAX III) that had a liquid nitrogen-cooled mercury cadmium telluride detector. The infrared radiation from a light source was passed into the silicon prism with an incident angle of 70° to enable total attenuation reflection at the electrode-solution interface.

The Si prism (20 mm in diameter, VeeMAX) was coated with a thin film of Au (~60 nm) using the electroless Au deposition method for surface enhanced infrared absorption spectroscopy.^[6] Prior to deposition, the Si prism was polished thoroughly with a 0.05 μm and 1.0 μm Al₂O₃ slurry (MicroPolish Alumina, Buehler), respectively, and sequentially cleaned with acetone, ethanol, and water via sonication. Silicon oxide was removed by immersing the Si surface in 40 wt% NH₄F for 2 min. The prism was then coated with a mixture of an Au plating solution (0.015 M NaAuCl₄·2H₂O + 0.15 M Na₂SO₃ + 0.05 M Na₂S₂O₃·5H₂O + 0.05 M NH₄Cl) and a 2 wt% HF solution in a 1:2 volume ratio at 70 °C for 3 min. After electroless Au coating, the surface was cleaned thoroughly with water and dried with N₂ gas. The Pd_xAc/C catalyst ink was prepared by sonicating 1 mg of catalyst and 10 μL of Nafion solution in 1 mL of isopropanol for 15 min. Then, 500 μL of Pd_xAc/C catalyst ink was sprayed on the Au-coated Si prism, which was assembled into a homemade electrochemical cell and used as a working electrode. The electrochemical cell was placed in the VeeMAX III ATR unit, and electrochemical measurements were carried out using a BioLogics SP-150e potentiostat. A Pt wire and Ag/AgCl (saturated 3 M NaCl) were employed as a counter electrode and a reference electrode, respectively. All spectroscopic measurements were acquired at a 4 cm⁻¹ spectral resolution with 16 scans, with a time resolution of ~6 s. The spectra were presented in absorbance, -log(R/R₀). For the time-dependent CO adsorption,

spectra were obtained at the $-0.2 V_{\text{RHE}}$ potential while the electrolytes were purged with CO for 15 min, followed by O₂ gas purging for 20 min. The applied potential during ORR was held for 1 min and the IR spectrum was obtained 50 s after applying the potential. O₂ gas was continuously purged during the measurement. The reference spectrum was taken at open circuit potential in Ar-saturated 0.1 M HClO₄.

2. Supplementary Table and Figures**Table S1.** Elemental composition determined by XRF and ICP-OES^a/ICP-MS^b

Catalyst	Pd loading (wt%)	Experimental Pd concentration (wt%)	Experimental carbon concentration (wt%)
		0.89 (0.87 ^a)	98.51
Pd ₁ Ac/C	1	0.47 (0.56 ^b)	98.22
		0.33 (0.33 ^b)	98.89
Pd ₂ Ac/C	2	1.49	97.74
Pd ₄ Ac/C	4	2.92	96.44

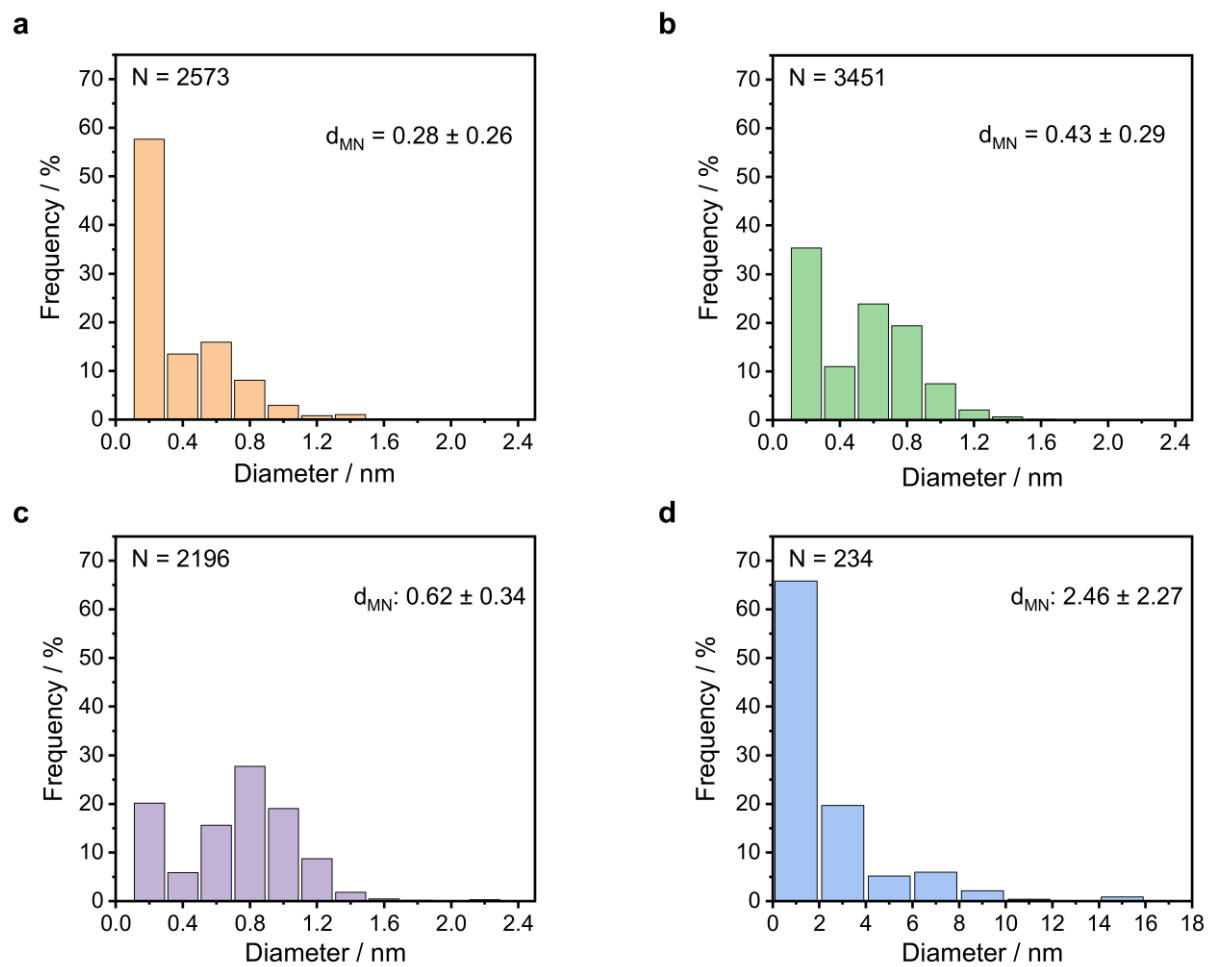


Figure S1. Particle size distribution of (a) Pd₁Ac/C, (b) Pd₂Ac/C, (c) Pd₄Ac/C, and (d) Pd_{NPs}/C.

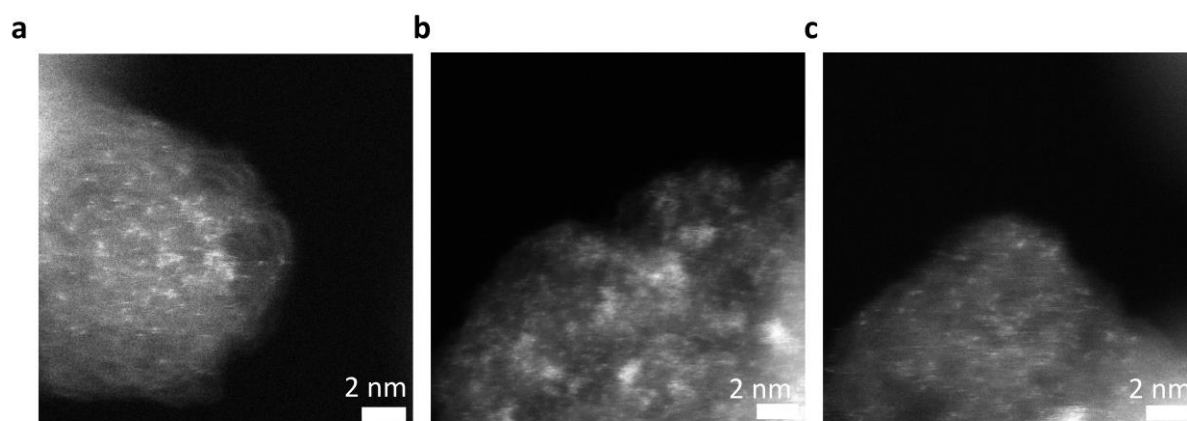


Figure S2. HRSTEM-HAADF images of samples with a Pd content of (a) Pd₁Ac/C, (b) Pd₂Ac/C, and (c) Pd₄Ac/C. Notice that Pd single atoms can be observed in all materials in the form of bright dots.

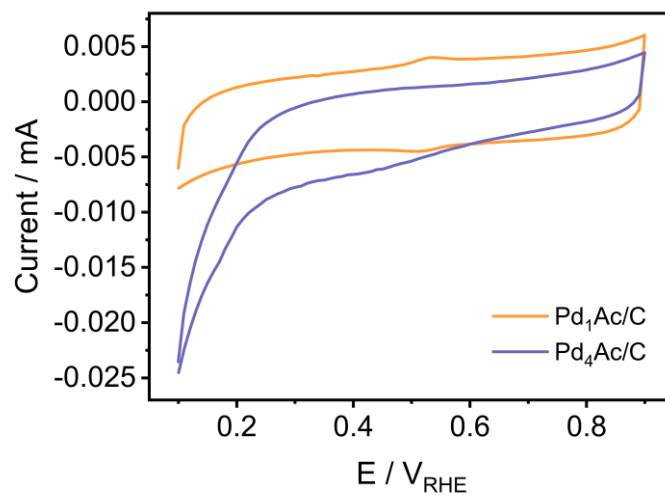


Figure S3. Initial current-potential curves of Pd₁Ac/C and Pd₄Ac/C obtained in 0.1 M HClO₄ electrolyte with a scan rate of 10 mV s⁻¹ between 0.1 and 0.9 V_{RHE} (end potential was 0.1 V_{RHE}) at 1600 rpm.

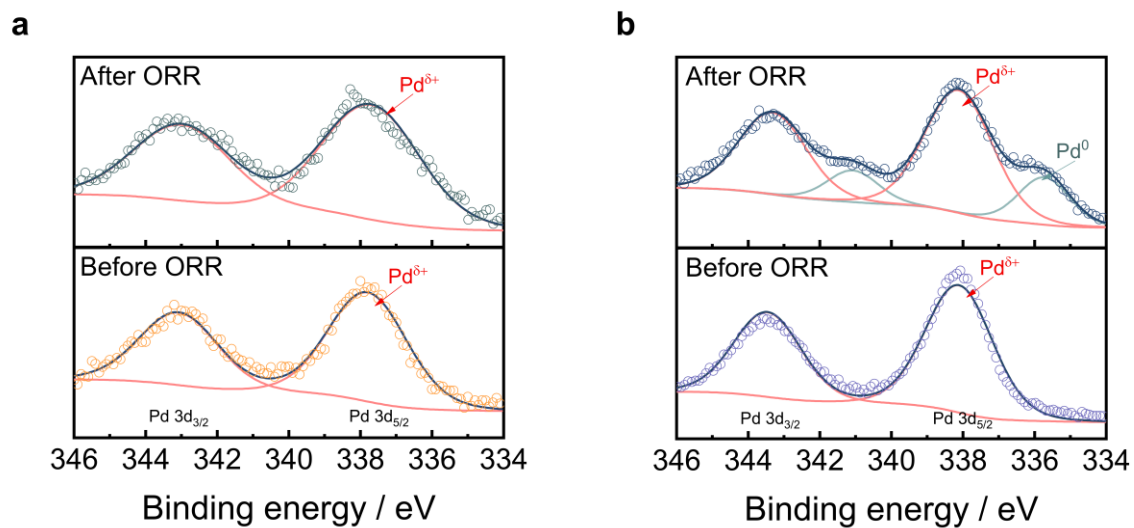


Figure S4. Core level of Pd 3d XPS spectra of (a) Pd₁Ac/C and (b) Pd₄Ac/C: before and after the CV with a scan rate of 10 mV s⁻¹ between 0.1 and 0.9 V_{RHE} (end potential was 0.1 V_{RHE}) in O₂-saturated 0.1 M HClO₄.

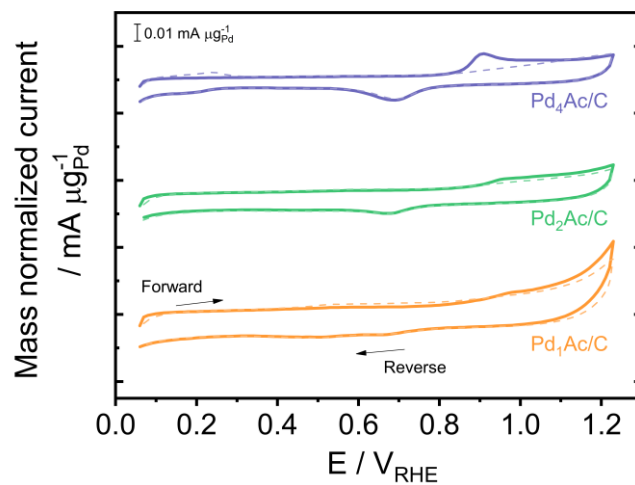


Figure S5. CO stripping voltammograms of Pd_xAc/C catalysts in N₂-saturated 0.1 M HClO₄ electrolyte. The CO stripping and N₂ background CV cycles are shown as solid curves and dashed curves, respectively.

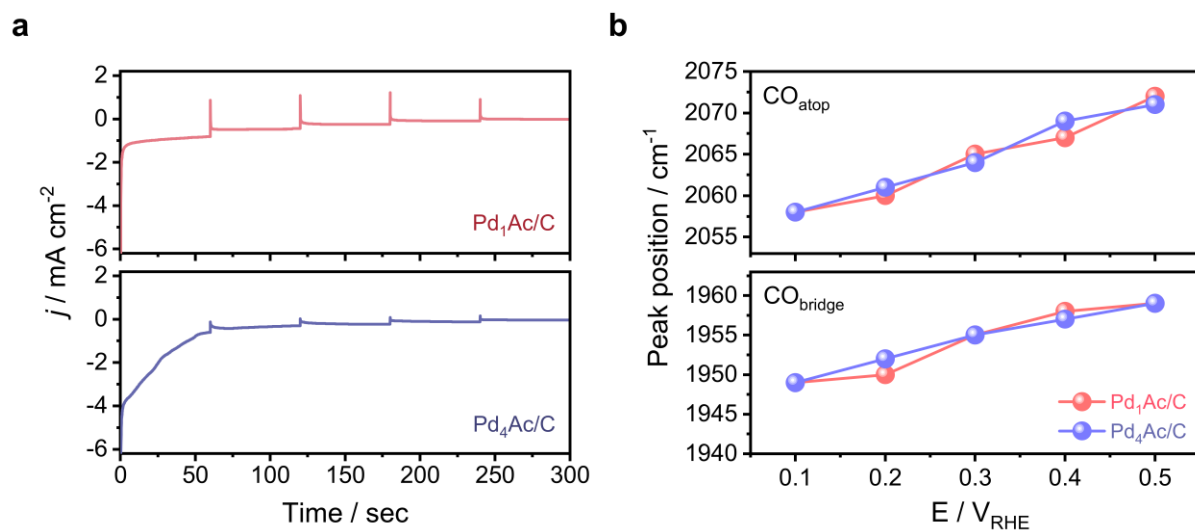


Figure S6. In-situ/operando EC ATR-SEIRAS analysis. (a) Current density during the in-situ/operando ATR-SEIRAS analysis for Pd₁Ac/C and Pd₄Ac/C after CO adsorption in O₂-saturated 0.1 M HClO₄. (b) The CO band frequency as a function of potential in the range of 0.1 to 0.5 V_{RHE}.

References

- [1] X. Sun, S. R. Dawson, T. E. Parmentier, G. Malta, T. E. Davies, Q. He, L. Lu, D. J. Morgan, N. Carthey, P. Johnston, S. A. Kondrat, S. J. Freakley, C. J. Kiely, G. J. Hutchings, *Nat. Chem.* **2020**, *12*, 560–567.
- [2] G. V. Fortunato, E. Pizzutilo, A. M. Mingers, O. Kasian, S. Cherevko, E. S. F. Cardoso, K. J. J. Mayrhofer, G. Maia, M. Ledendecker, *J. Phys. Chem. C* **2018**, *122*, 15878–15885.
- [3] U. A. Paulus, T. J. Schmidt, H. A. Gasteiger, R. J. Behm, *J. Electroanal. Chem.* **2001**, *495*, 134–145.
- [4] Y. Sun, I. Sinev, W. Ju, A. Bergmann, S. Dresp, S. Kühl, C. Spöri, H. Schmies, H. Wang, D. Bernsmeier, B. Paul, R. Schmack, R. Kraehnert, B. Roldan Cuenya, P. Strasser, *ACS Catal.* **2018**, *8*, 2844–2856.
- [5] O. Antoine, R. Durand, *J. Appl. Electrochem.* **2000**, *30*, 839–844.
- [6] H. Miyake, S. Ye, M. Osawa, *Electrochem. commun.* **2002**, *4*, 973–977.

Author Contributions

J. S. Choi designed and performed the experiments, analyzed data, and wrote the manuscript in consultation with M. Ledendecker, Y. J. Hwang and G.V. Fortunato; S. Yoo performed and analyzed the in-situ/operando EC ATR-SEIRAS; E. S. Koh, R. Aymerich-Armengol, and C. Scheu performed and analyzed STEM; G. V. Fortunato and M. R.V. Lanza aided in interpreting the results and worked on the manuscript; Y. J. Hwang and M. Ledendecker supervised the project. All authors discussed the results and commented on the manuscript.