

Supporting Information Available:

Raman Analysis of Mode Softening in Nanoparticle CeO_{2-δ} and Au-CeO_{2-δ} during CO Oxidation

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1. Residual gas analysis of flow after passing over ceria nanoparticles

Figure S1 shows the mass 44 signal of CO₂ measured in the residual gas analyzer (RGA) after CO flow over ceria nanoparticles during heating and cooling cycles for a variety of conditions. The temperature was increased to 25 °C intervals from 0 to 100 °C and to 100 °C intervals afterwards. Between intervals the heating/cooling rate was 50 °C/min. The temperature was kept constant at the intervals for 10 min.

Figure S1a shows the relative CO reactivities for different shapes of particles. Figure S1b shows the change in reactivity for different flow mixtures. The production of CO₂ increases when O₂ gas is incorporated into the gas flow.

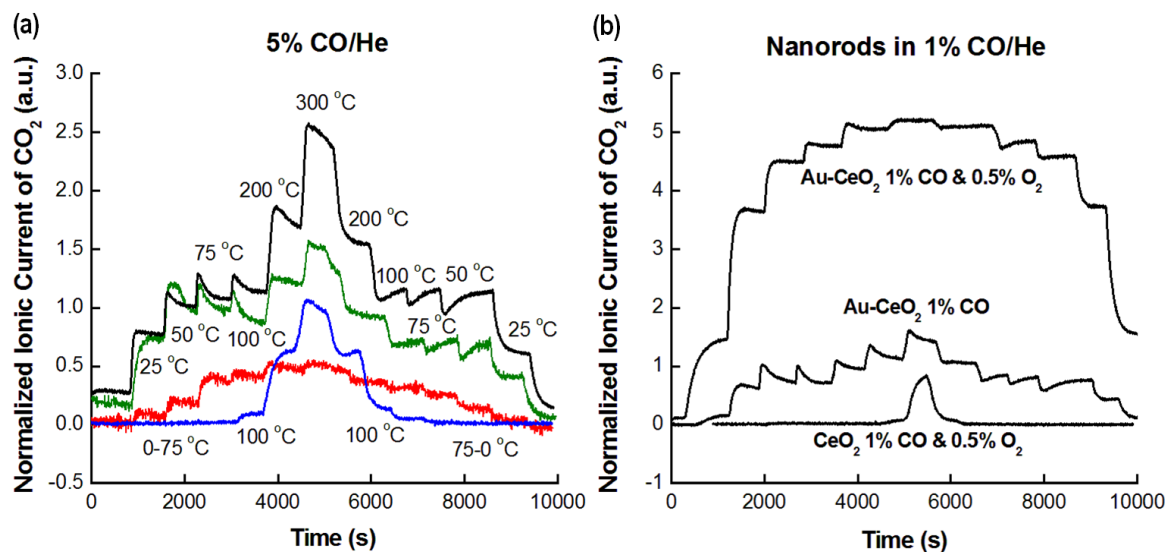


Figure S1. RGA results showing CO₂ (mass 44) product at various temperatures. (a) CeO₂ nanorods (blue), Au-CeO₂ nanorods (black), Au-CeO₂ polyhedra (green), and Au-CeO₂ cubes (red) with the same flow condition (20 sccm, 5% CO/He) and (b) CeO₂ and Au-CeO₂ nanorods with 1% CO/0.5% O₂/He flow and Au-CeO₂ nanorods with 1% CO/He flow. The arbitrary units are the same in both parts.

2. Reaction pathways of CO oxidation

Figure S2 shows RGA analysis of the gas effluent during the CO oxidation by Au-CeO₂ nanorods with (a) 5% CO/He and (b) 1% CO/0.5% O₂/He flow with O₂ and H₂ (and in part (b) also CO) monitored in addition to the CO₂ product during the heating and cooling cycle.

The temperature ranges of the three major reaction pathways of CO oxidation on the surface are also shown in part (a): (I) the gas phase reaction $\text{CO (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)}$, which starts at low temperatures (the “lights-off” temperature) (< 50 °C); (II) oxidation by lattice oxygen of CeO₂, which starts at intermediate temperatures (50-100 °C); and (III) the

water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$), which starts at higher temperatures ($>200^\circ\text{C}$).

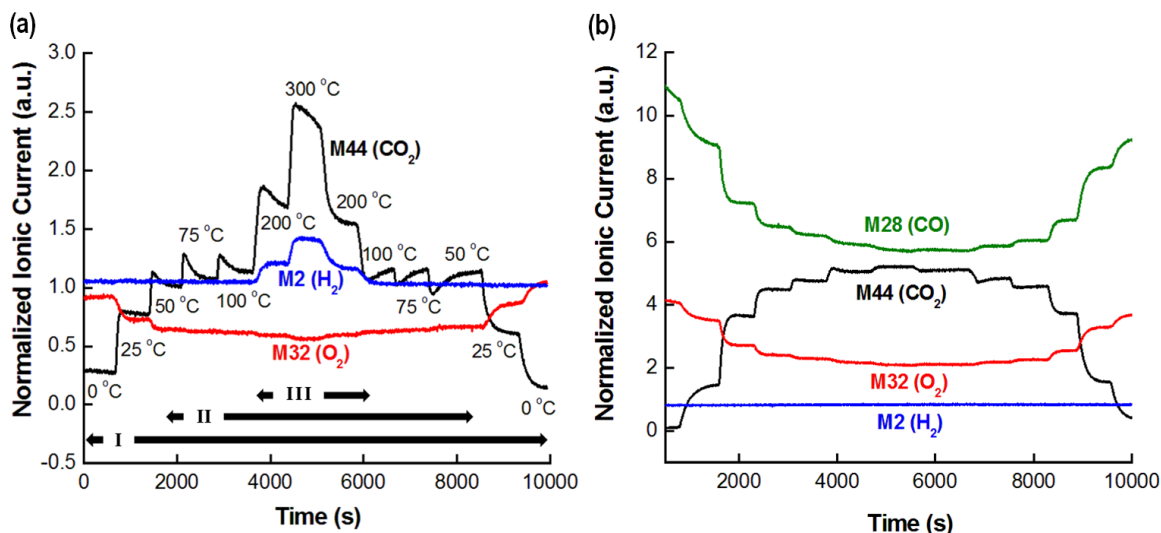


Figure S2. RGA results showing effluent CO₂ (mass 44), O₂ (32), and H₂ (2) during the heating and cooling of Au-CeO₂ nanorods with (a) 5% CO/He and (b) 1% CO/0.5% O₂/He flow (also with CO, mass 28, in part b). Part (a) also shows the temperature ranges of the three major reaction pathways of CO oxidation on the surface: (I): the gas phase reaction $\text{CO} (\text{g}) + 1/2 \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g})$, starting at low temperatures ($< 50^\circ\text{C}$); (II) oxidation by lattice oxygen of CeO₂, starting at intermediate temperatures (50-100 $^\circ\text{C}$); and (III) the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$), starting at higher temperatures ($>200^\circ\text{C}$). Due to the presence of O₂ flow in part (b), the major reaction over the whole temperature range is gas phase reaction (I).

In part (a), with 5% CO/He flow, CO₂ production at 0 and 25 $^\circ\text{C}$, with no concomitant decrease of the CO₂ product with time, suggests the importance of reaction I, due to trace levels of O₂. Because lattice oxygen is not the source of CO oxidation during reaction I, there is no net increase in oxygen vacancies and no change in the Raman shift

relative to that with inert gas flow at these low temperatures (Figure 2), even though there is considerable CO₂ production.

At higher temperatures, in addition to the increase in the CO₂ product, there is a decrease in CO₂ production with time, at each targeted temperature during the heating cycle, starting at 50 °C. This indicates the onset of reaction II (which occurs in addition to reaction I), during which lattice oxygen is consumed with simultaneous CO oxidation and CeO₂ reduction, resulting in the formation of oxygen vacancies. This suggestion of the depletion of surface oxygen by RGA starting at 50 °C coincides with the onset of the deviation of the Raman shift from those taken with inert gases flowing (Figure 2).

At higher temperatures (200 and 300 °C), the production of CO₂ increases and H₂ is clearly detected, indicating that the third route of CO oxidation begins, the water-gas shift reaction (reaction III), due to trace water vapor. At these targeted temperatures, there is still a decrease in CO₂ product with time (though it is slower than that from 50-100 °C) due to some regeneration of surface oxygen due to the trace H₂O (in addition to that due to trace O₂).

While the three major reactions are clear during the temperature cycle with 5% CO/He flow over Au-CeO₂ nanorods, the only observable CO oxidation reaction pathway with 1% CO/0.5% O₂/He flow is gaseous CO oxidation with O₂ (reaction I), with no significant decrease in CO₂ production seen at the targeted temperatures or any increase in H₂ production.

3. Raman analysis

Figure S3 shows details of the shifts and widths (FWHM) of the Raman F_{2g} peak for CeO_2 and Au- CeO_2 nanorods with He and 5% CO/He flow. The usual decrease in Raman shift and increase in Raman width with increasing temperature is seen. There are only small differences in peak positions during heating and cooling, which suggests that oxygen depletion in the Figure S3(d) run decreases during cooling due to trace H_2O and O_2 .

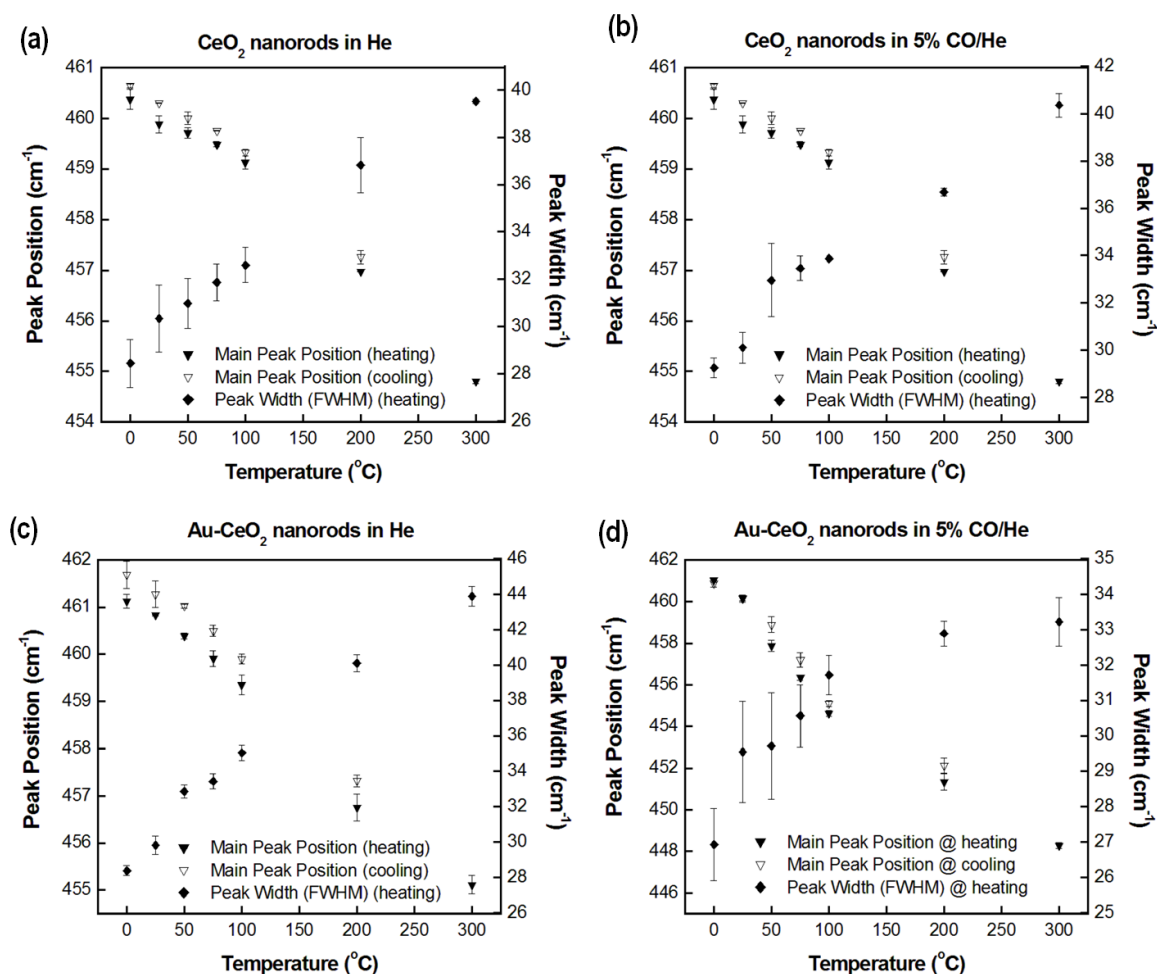


Figure S3. Analysis of the main Raman peak of CeO_2 and Au- CeO_2 nanorods in He and 5% CO/He, as described in the main text and in Figure S1. The peak positions are shown during the heating and cooling cycles, and peak widths are shown during the heating cycle.

In Figure 1 several of the small Raman peaks are seen to depend on temperature and reaction conditions. The peak near 260 cm^{-1} is usually attributed to 2TA or the doubly degenerate TO mode, which is Raman inactive in a perfect crystal.¹ With He and 5% CO/He flow, it is observed in CeO_2 nanorods, Au- CeO_2 nanorods, and Au- CeO_2 polyhedra over a wide range of temperature, and in bulk CeO_2 at and above $200\text{ }^\circ\text{C}$, but it is always very small in Au- CeO_2 nanocubes. Relative to the main Raman peak, this peak is smaller in the bulk than in the rods, and its strength increases with temperature in the bulk, as is expected from these mode assignments. However, in Au- CeO_2 rods and polyhedra, it becomes weaker relative to the main peak as temperature is increased and it finally disappears at $200\text{ }^\circ\text{C}$ in 5% CO/He flow, but not in 1%CO/0.5% O_2 /He or He flow. This suggests that there may also be a peak near 260 cm^{-1} due oxygen-containing species on the surface that disappears upon oxygen depletion or the mode becomes less Raman active due to oxygen depletion.

Figure 3 plots the shift and normalized area of the defect mode feature near 600 cm^{-1} . This feature includes contributions from intrinsic defects and oxygen vacancies.

The peroxide peak ($\sim 830\text{ cm}^{-1}$) originates at the isolated two-electron surface defect sites and is strong when the gas phase reaction of CO with O_2 (reaction regime I) is active.² It is consequently particularly strong on the Au- CeO_2 rod and polyhedra surfaces, but weak on the CeO_2 rod surface. With 5% CO/He flow, this peak disappears due to the reaction of the peroxide surface lattice oxygen, near $50\text{ }^\circ\text{C}$ on Au- CeO_2 and at over $100\text{ }^\circ\text{C}$ on CeO_2 . In the presence of O_2 flow (1%CO/0.5% O_2 /He), the peak on Au- CeO_2 rods is visible up to

100 °C. It is seen but is very weak in CeO₂ rods, Au-CeO₂ rods, and Au-CeO₂ polyhedra in He flow.

A very broad peak is observed near 760 cm⁻¹ in Au-CeO₂ rods and polyhedra with 5% CO/He flow at elevated temperature, after the peroxide peak has disappeared. The peak near 1050 cm⁻¹ is strong in all Au-CeO₂ samples, both with He and 5% CO/He flow. The intensity of the 1050 cm⁻¹ peak increases relative to the second order peak at 1170 cm⁻¹ as the rate of CO oxidation is increased. This peak also appears in CeO₂ rods at 300 °C in 5% CO/He flow, after about an hour, and then disappears upon cooling.

The peak near 1050 cm⁻¹ has been attributed to residual peaks from chemical species during the chemical synthesis. However, this peak becomes stronger in Au-CeO₂ samples during CO oxidation at higher temperatures (with no O₂ flowing), and therefore it may also be related to the creation of oxygen defect sites and, in particular, to the stretching mode associated with the short terminal Ce=O.³ These oxygen defect sites may also lead to antisymmetric Ce-O-Ce or symmetric O-Ce-O vibrations that would produce the 760 cm⁻¹ peak.³

Further studies are underway to clearly identify these weaker peaks, and these results will be reported in a subsequent publication.

References

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