

Supporting Information Description

Ce 3d XPS peak fitting:

Ce 3d XPS region can contain 10 peaks originated from different Ce oxidation states (Ce^{3+} and Ce^{4+}) and their 4f configurations; therefore it can be used to determine the percent contributions of Ce^{3+} and Ce^{4+} ions in the grown $\text{CeO}_x(111)$ film. In our study, the Ce 3d XPS spectrum from each grown film was fitted by linear combination of the reference spectra from stoichiometric ceria samples (CeO_2 and $\text{CeO}_{1.5}$) using the formula $[\text{CeO}_x] = y*[\text{CeO}_2] + (1-y)*[\text{CeO}_{1.5}]$ since the CeO_2 and $\text{CeO}_{1.5}$ samples have pure Ce^{4+} and Ce^{3+} species. All the Ce 3d spectra for the film of interest as well as two reference samples were collected with the same XPS settings including the binding energy range (923-870 eV) and the total data points (2650). Here, [sample] is the Ce 3d XPS intensity for each binding energy data point. y and $1-y$ are percent contributions for Ce^{4+} and Ce^{3+} ions, respectively. This formula can calculate a projected $[\text{CeO}_x]$ intensity for every data point in the spectrum, and thus the absolute difference between this value and the actual experimental $[\text{CeO}_x]$ intensity at that binding energy can be found. Using Newton's method, the sum of these differences is minimized using y as a variable while subjected to the constraint $0 \leq y \leq 1$ and the optimal value of y can be obtained. The value x can be calculated using the formula $x = 2*y + 1.5*(1-y)$. Prior to peak fitting, the intensities of all the XPS spectra from the ceria thin films, CeO_2 , and $\text{CeO}_{1.5}$ are normalized after the background subtraction. Furthermore, their baselines are aligned with respect to each other. The fitting program was written in-house using Visual Basic for Applications. Shown in Panel a (Figure SI-1) is an example for the fitting of the reduced ceria thin film grown with an oxygen pressure of 8×10^{-8} Torr. The optimum value for y is 76% and x is determined to be 1.88. Thus the film is designated as $\text{CeO}_{1.88}$. Similarly, the other two ceria thin films grown with oxygen pressures of 2×10^{-7} and 2×10^{-8} Torr can be determined to be CeO_2 and $\text{CeO}_{1.77}$. The standard deviation of y determined from this peak fitting method is less than 2%.

The linear combination method of peak fitting of the Ce 3d spectrum for the grown ceria film was compared to the peak decomposition method using the Fityk curve fitting program in the study. As shown in Panel b (Figure SI-1), the Ce 3d spectrum can be fitted with 5 sets of spin-orbit split doublets of Ce 3d ($3d_{5/2}$ and $3d_{3/2}$) with a Gaussian-Lorentzian peak shape after the subtraction of a Shirley-type background. The detailed information about these 10 fitted peaks can be found in the attached table (Table SI-1). To ensure proper peak fitting, the area ratio of 3d spin-orbit split doublets, their splits, as well as peak positions and their FWHMs from the reference spectra were considered. With this method, the percent concentration of Ce^{4+} ions in the film can be calculated from the ratio of the sum of the

integrated areas of the XPS 3d peaks related to Ce^{4+} to the total integral area for the whole Ce 3d region. As demonstrated in our data, fitting of the reduced ceria thin film grown with an oxygen pressure of 8×10^{-8} Torr using the peak decomposition method results in the y value of 78% and the x value of 1.89, which agrees well with values obtained using the linear combination method. Therefore, the simple linear combination method is used as the main peak analysis method for the study.

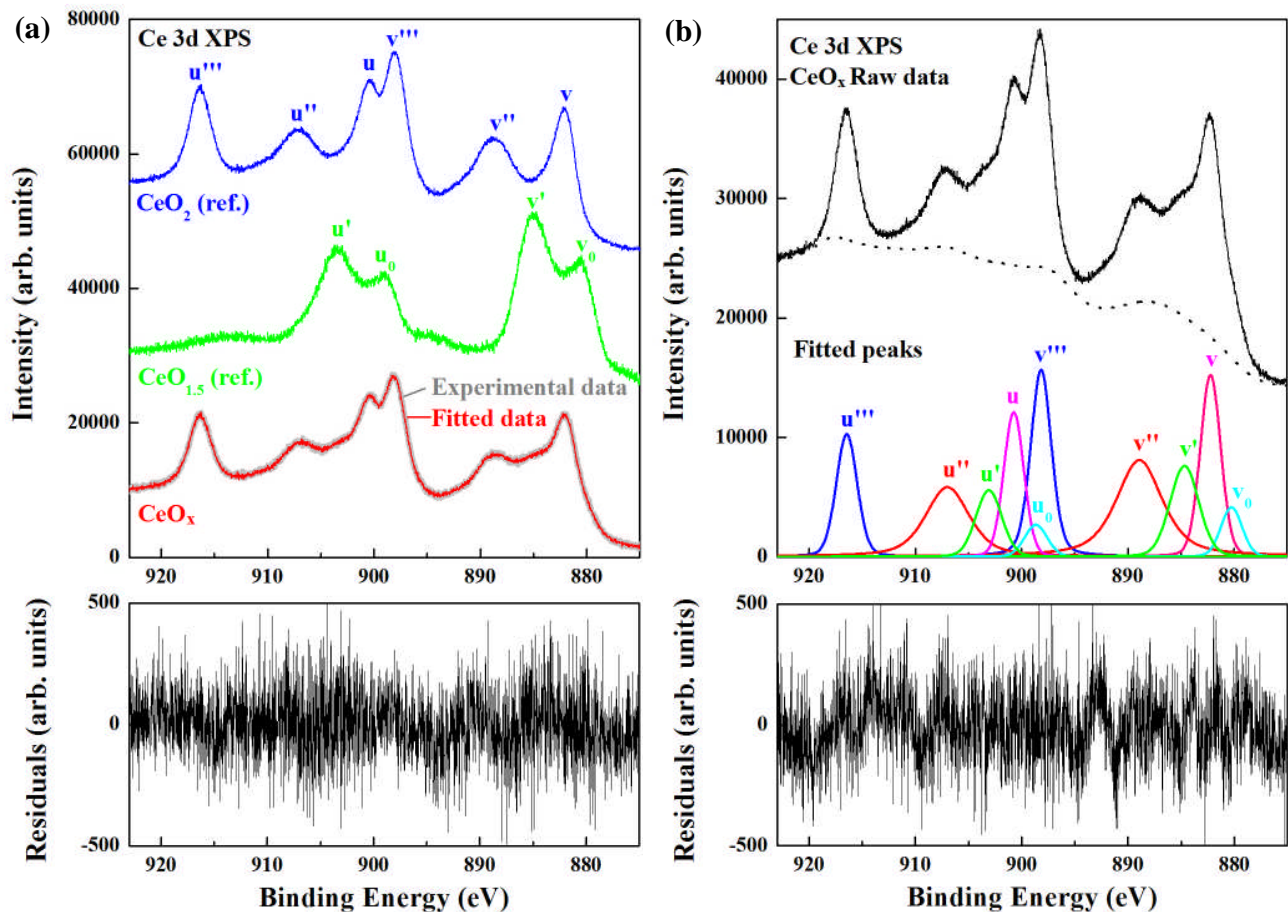


Figure SI-1. Curve-fitting for Ce 3d XPS spectrum collected from the reduced CeO_x thin film grown with an oxygen pressure of 8×10^{-8} Torr by (a) linear combination and (b) Gaussian-Lorentzian peak decomposition methods. Panel a shows Ce 3d XPS spectra for CeO_2 (blue line), $\text{CeO}_{1.5}$ (green line), as well as the grown CeO_x thin film (grey line), the intensities of which are normalized after the background subtraction. The fitted Ce 3d spectrum (red line) is overlaid on top of the experimental data. In panel b, the raw experimental Ce 3d spectrum is shown on top. Shirley-type background (dotted line) was used to remove the background from the spectrum before the peak fitting. The fitted 5 sets of spin-orbit split doublets of Ce 3d ($3d_{5/2}$ and $3d_{3/2}$) are displayed in the panel. More detailed information about these peaks can be found in Table SI-1. For each fitting, the remaining residual signal is also shown.

Table SI-1. Peak position, full width at half maximum (FWHM), and integrated peak area of the fitted 5 sets of spin-orbit split doublets of Ce 3d ($3d_{5/2}$ and $3d_{3/2}$) from a grown $\text{CeO}_x(111)$ film shown in Figure SI-1b. The percentage of Ce^{4+} cations in the film is listed. The origin of these ten peaks as well as their reference positions from the stoichiometric CeO_2 and $\text{CeO}_{1.5}$ samples are also listed.

Peak assignment	Origin of cerium contribution	Reference peak position from CeO_2 and $\text{CeO}_{1.5}$ samples	Peak decomposition		
			Peak	FWHM	Area
u'''	Ce^{4+}	916.3	916.4	2.3	27465
u''	Ce^{4+}	907.0	907.0	4.9	37478
u'	Ce^{3+}	903.3	903.1	2.9	17945
u	Ce^{4+}	900.5	900.7	2.2	30075
u ₀	Ce^{3+}	898.9	898.6	2.5	7522
v'''	Ce^{4+}	898.0	898.1	2.3	42277
v''	Ce^{4+}	888.6	888.7	5.1	56926
v'	Ce^{3+}	884.9	884.7	3.2	27575
v	Ce^{4+}	882.1	882.2	2.3	39016
v ₀	Ce^{3+}	880.5	880.2	2.4	10913
$\text{Ce}^{4+}\%$					78%
x in CeO_x					1.89

Pt 4f XPS peak fitting:

Pt 4f XPS region with a binding energy range between 65 and 85 eV collected from CeO₂ upon 0.2 ML Pt deposition at 300 K (top purple line) is shown in Figure SI-2, which is used as an example to describe the peak fitting of the Pt 4f spectrum. It overlaps with the 4s peak from the Ru substrate. The contribution of Ru from the Pt region was removed using a background spectrum with the same binding energy range collected from the ceria surface prior to the Pt deposition (middle blue line). The resulted Pt 4f spectrum indicated as magenta scattered dots can be fitted with one set of spin-orbit split doublets of Pt 4f (4f_{5/2} and 4f_{7/2}, black dashed lines) that are 3.3 eV apart using a asymmetric Pearson7 function in the fityk software. The fitted Pt 4f spectrum (magenta line) agrees well with the original spectrum. This procedure was used for curve-fitting of the remaining Pt 4f XPS spectra. Figure SI-3 display all the fitted Pt 4f spectra (solid lines) from three Pt/CeO_x surfaces at 300 K as well as after heating to higher temperatures (500 K, 700 K, and 800 K). Detailed information about the spin-orbit split doublets of Pt 4f (4f_{7/2} and 4f_{5/2}, black dashed lines) are tabulated in Table SI-2.

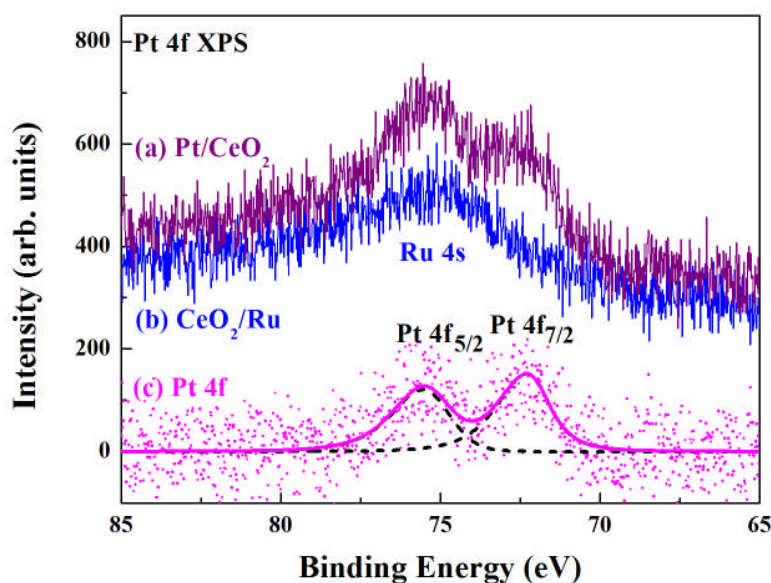


Figure SI-2. (a) Pt 4f region obtained after room-temperature deposition of 0.2 ML Pt onto a CeO₂(111) thin film grown on Ru (purple, top); (b) The background spectrum collected from the CeO₂/Ru surface before Pt deposition (blue, middle); (c) The Pt 4f experimental data (magenta scattered dots) as well as fitted Pt 4f spectrum (solid magenta line) and spin-orbit split doublets of Pt 4f (4f_{7/2} and 4f_{5/2}) (black dashed lines).

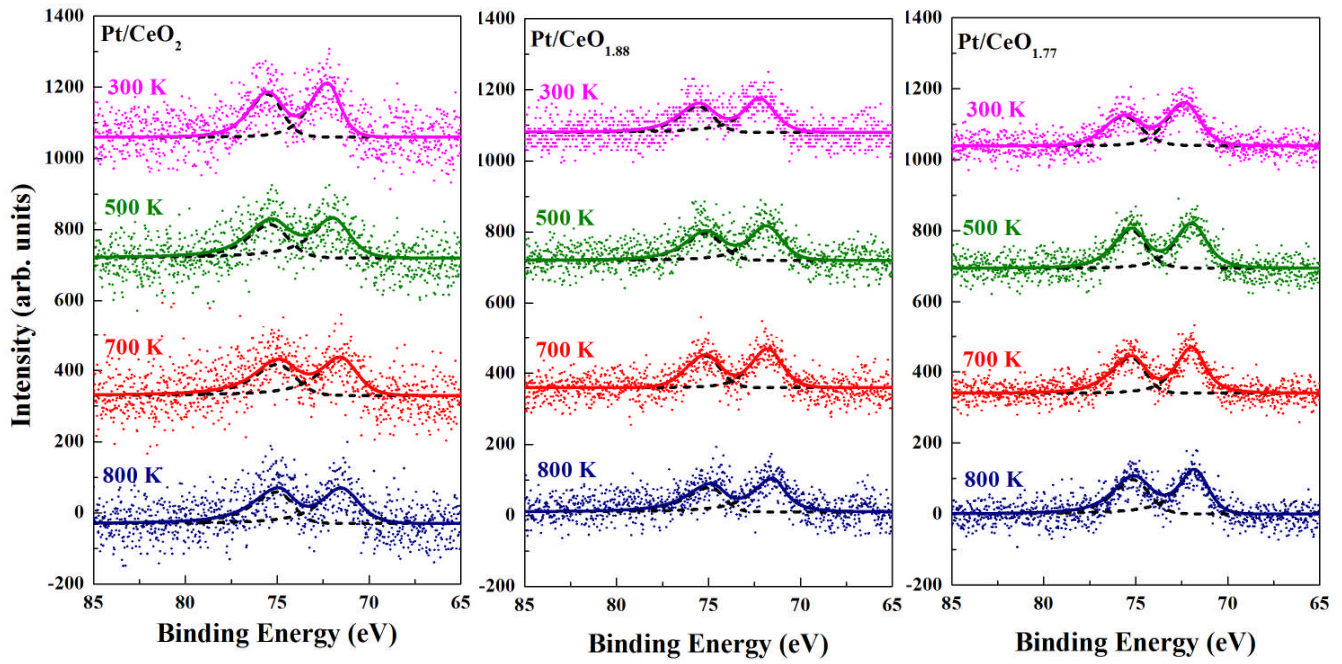


Figure SI-3. Curve-fitting for Pt 4f XPS spectra of Pt/CeO_x surfaces after Pt deposition at 300 K and annealing to higher temperatures. All Pt spectra (scattered dots) used for peak fitting are after the subtraction of the substrate Ru 4s signal.

Table SI-2. Peak position, full width at half maximum (FWHM) of fitted Pt 4f_{7/2} and 4f_{5/2} peaks from three Pt/CeO_x surfaces.

	Pt/CeO ₂				Pt/CeO _{1.88}				Pt/CeO _{1.77}			
	Pt 4f _{7/2}		Pt 4f _{5/2}		Pt 4f _{7/2}		Pt 4f _{5/2}		Pt 4f _{7/2}		Pt 4f _{5/2}	
	Peak	FWHM	Peak	FWHM	Peak	FWHM	Peak	FWHM	Peak	FWHM	Peak	FWHM
300 K	72.3	1.9	75.6	2.2	72.3	2.0	75.6	2.2	72.3	2.1	75.6	2.3
500 K	72.0	2.4	75.4	2.6	71.9	2.1	75.2	2.3	71.9	2.0	75.2	2.2
700 K	71.6	2.4	75.0	2.6	71.8	2.0	75.1	2.2	71.9	1.9	75.2	2.2
800 K	71.5	2.5	74.9	2.6	71.5	2.1	74.9	2.3	71.8	1.9	75.1	2.3