SUPPORTING INFORMATION

Local Structure and Electronic State of Atomically Dispersed Pt Supported on Nanosized CeO_2

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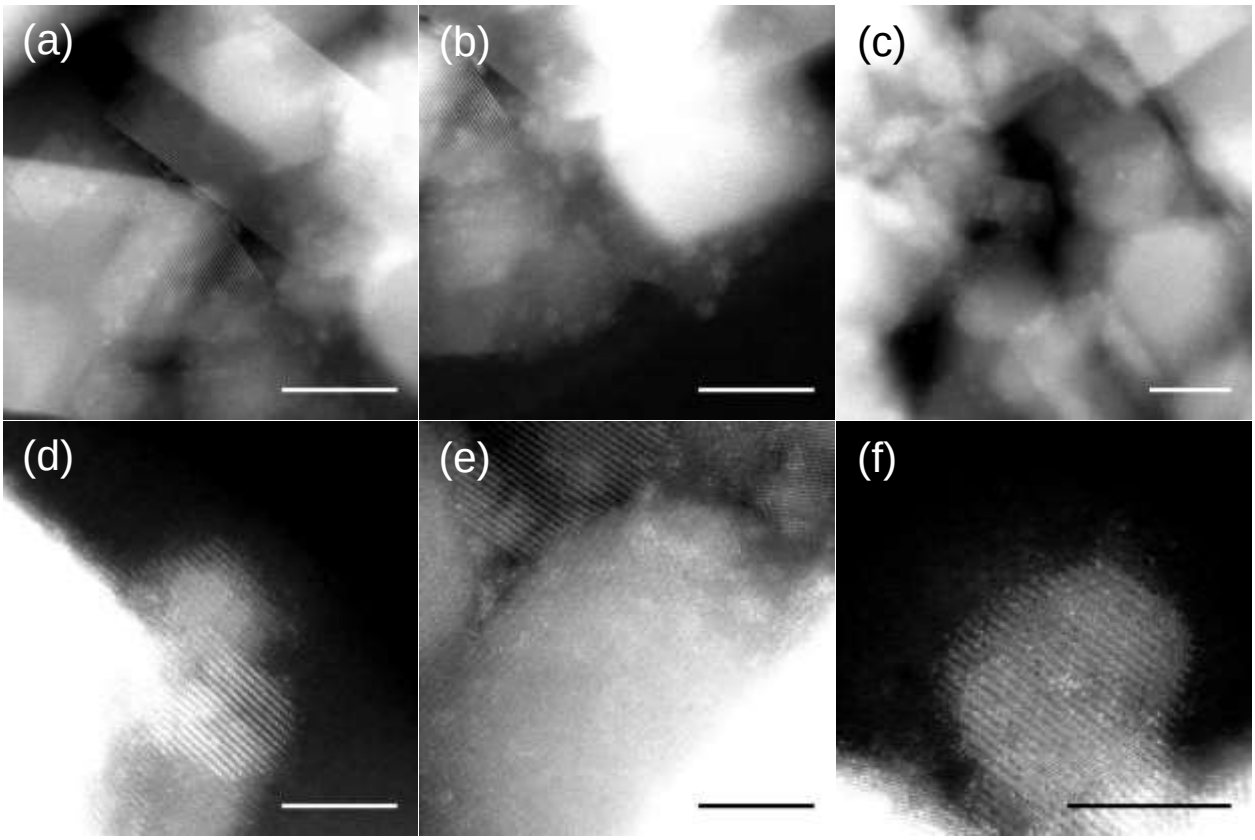

Figure S1. Additional STEM images of PtO_x clusters deposited on CeO_2 (a-c) and Pt single atoms deposited on CeO_2 (d-f). Scale bars are 10 nm (a-c) and 5 nm (d-f).

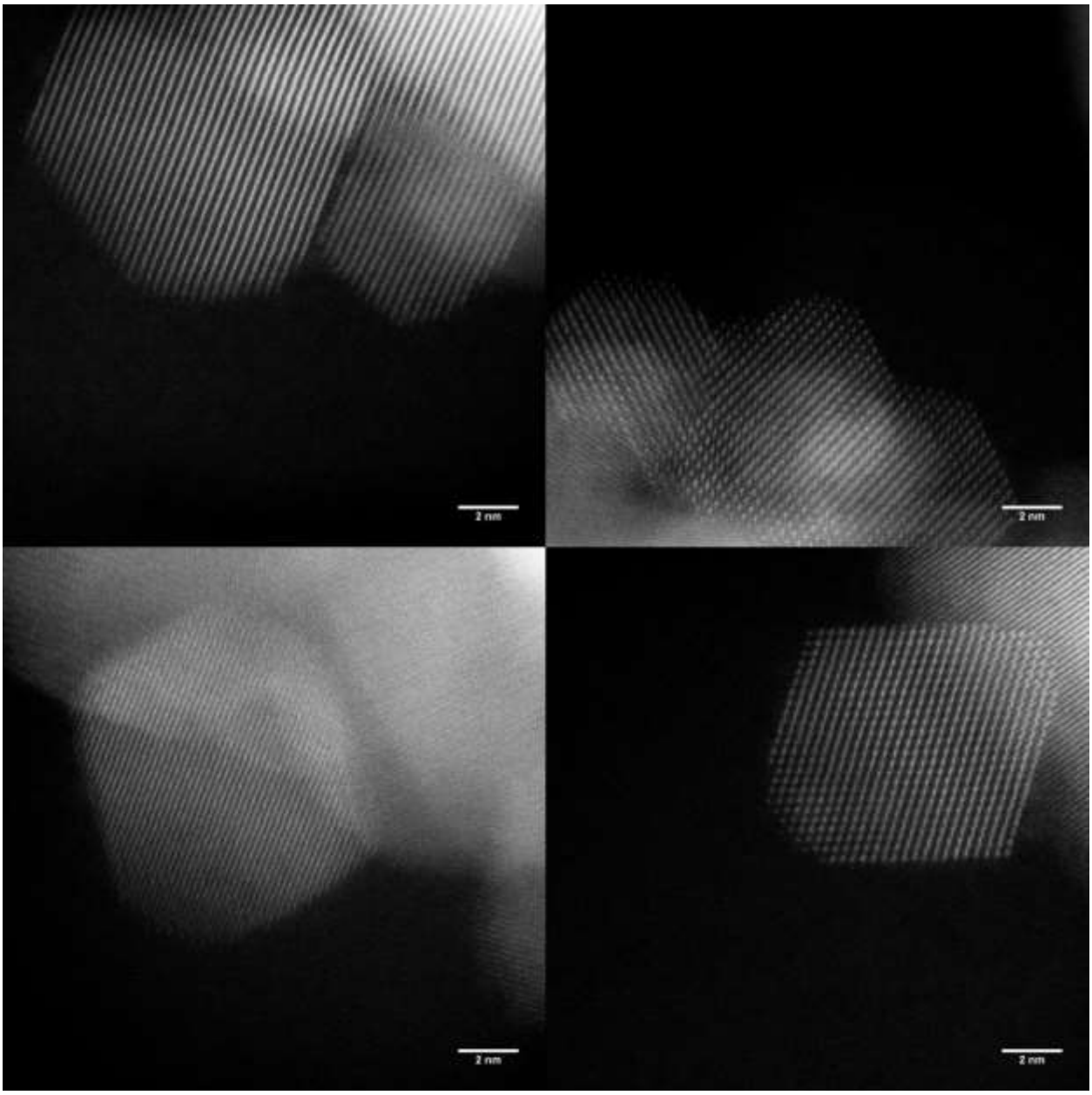

Figure S2. STEM images of a sample prepared via the sol-gel-based synthesis with the Pt precursor excluded.

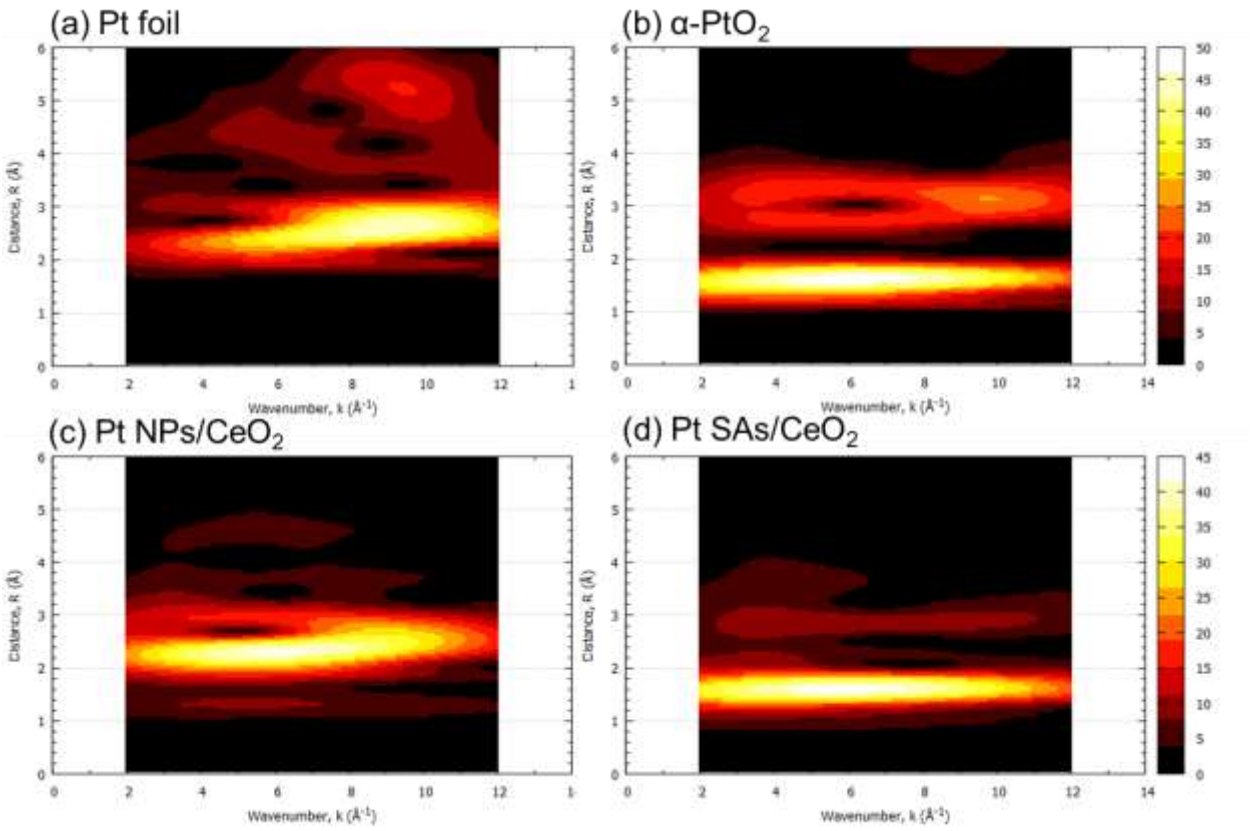

Figure S3. Wavelet Transform (WT) – EXAFS of (a) Pt foil, (b) α-PtO_2, (c) Pt NPs/CeO_2, and (d) Pt SACs/CeO_2 data. The comparison shows the similarity between the WT-EXAFS map of Pt NPs/CeO_2 and Pt foil and the uniqueness of Pt SACs/CeO_2.

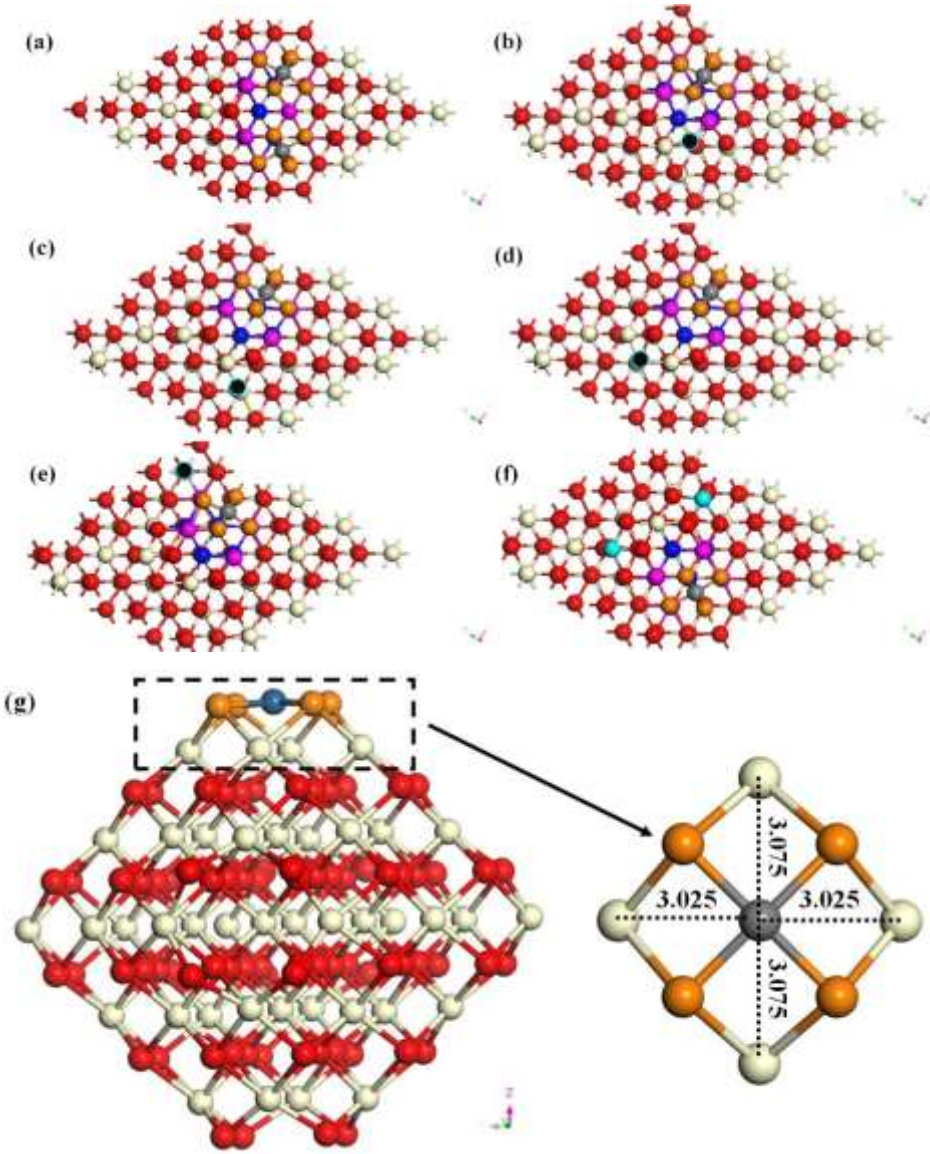

Figure S4. Top views of six slab models containing a small ceria cluster mimicking the {100} nanofacets on the ceria (111) surface as well as a cluster model. The unit cell contains two Pt atoms (Pt_2/CeO_2) (a), one Pt atom and one oxygen vacancy on three different locations of the ceria {100} cluster ($Pt\text{-}O_{V1}/CeO_2$, $Pt\text{-}O_{V2}/CeO_2$, and $Pt\text{-}O_{V3}/CeO_2$) (b-d), one Pt atom and one oxygen vacancy on the ceria (111) surface ($Pt\text{-}O_{SV}/CeO_2$) (e), one Pt atom and two reduced Ce atoms ($Pt\text{-}2Ce^{3+}/CeO_2$) (f), and the $PtCe_{40}O_{80}$ nanoparticle (g) respectively. Red, white, gray and light blue balls represent O, Ce, Pt and trivalent Ce atoms, respectively. Orange, pink and blue balls represent the top-layer O atoms in the first shell, the top-layer Ce atoms in the second shell, and the second-layer O atoms in the third shell of the Pt atoms, respectively. In (b)-(e), Black spheres represent the O vacancy.

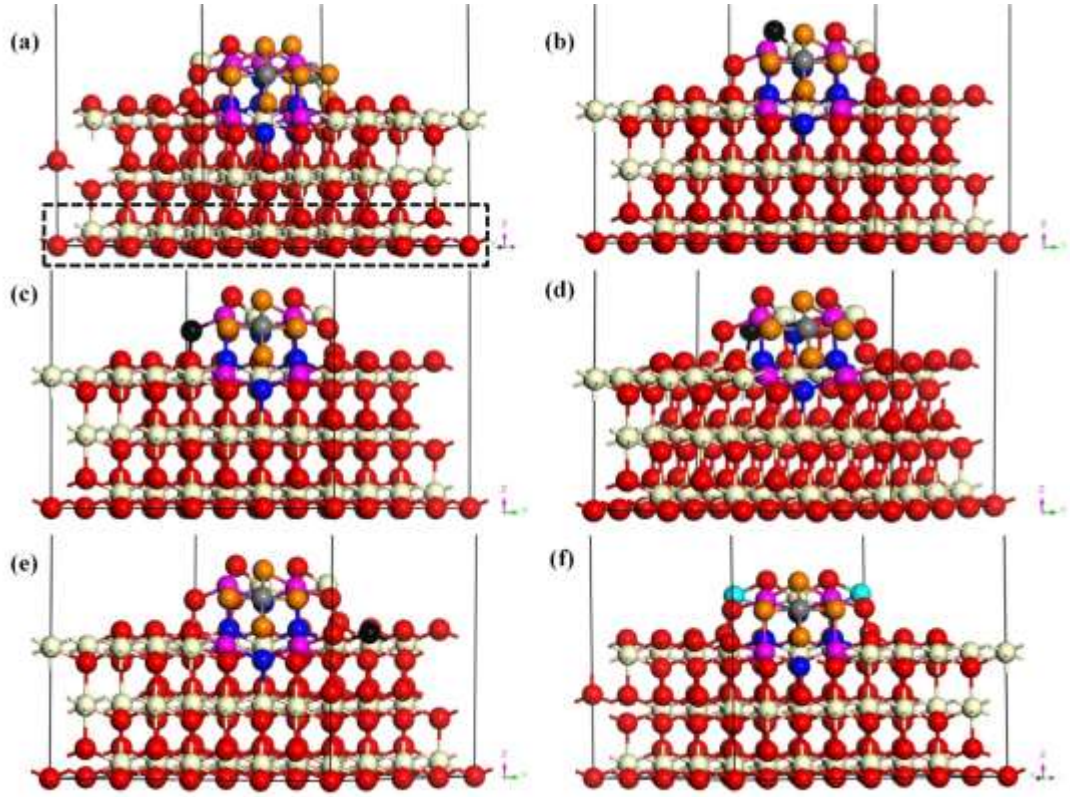

Figure S5. Side views of the same slab models in Figure S4. The dashed rectangular box in (a) indicates the bulk region of CeO_2, where atoms are fixed during the structure optimization.

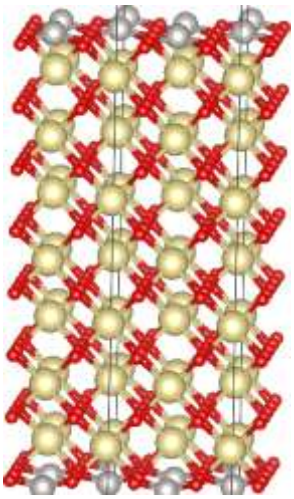

Figure S6. Structure model of the Pt passivated CeO_2(100) surface. Solid lines indicate the unit cell.

Table S1. The average Pt-O bond length (d_{Pt-O}, Å) between the platinum atom and the first-shell O atoms, the average Pt-Ce distance (d_{Pt-Ce}, Å) between the platinum atom and the second-shell Ce atoms, and the Bader charge (BC) of platinum atoms on the surface of Pt_2/CeO_2, $Pt\text{-}O_{V1}/CeO_2$, $Pt\text{-}O_{V2}/CeO_2$, $Pt\text{-}O_{V3}/CeO_2$, $Pt\text{-}O_{sv}/CeO_2$ and $Pt\text{-}2Ce^{3+}/CeO_2$ model. Values in the parentheses (Δ, %) are the percentage deviation of the theory with respect to the corresponding experimental values.

Model	**$d_{Pt-O}(\Delta)$**	**$d_{Pt-Ce}(\Delta)$**	**Bader Charge**
Experiment	1.995	3.34	
Pt_2/CeO_2*	2.028(1.65)	3.075(-7.93)	0.888/0.919
$Pt\text{-}O_{V1}/CeO_2$	2.028(1.65)	3.073(-7.99)	1.103
$Pt\text{-}O_{V2}/CeO_2$	2.026(1.55)	3.075(-7.93)	0.876
$Pt\text{-}O_{V3}/CeO_2$	2.027(1.57)	3.081(-7.75)	0.782
$Pt\text{-}O_{sv}/CeO_2$	2.030(1.75)	3.075(-7.93)	0.966
$Pt\text{-}2Ce^{3+}/CeO_2$	2.027(1.50)	3.072(-8.02)	0.862
PtO			0.944
PtO_2			1.770

* The two platinum atoms in this model have the same structural parameters, but slightly different Bader charge.

Table S2. Formation energies pertinent to the stability of the $Pt_4/O_4/CeO_2(100)$ model. With these energies, we calculate two formation energies per Pt atom: ¼(E[$Pt_4/O_4/CeO_2(100)$] – E[$CeO_2(100)$] – 2*E[PtO bulk (Pt_2O_2)]) = -0.52 eV; ¼(E[$Pt_4/O_4/CeO_2(100)$] – E[$CeO_2(100)$] – E[Pt bulk (Pt_4)]/2 - E[PtO_2 bulk (Pt_2O_4)]) = -0.28 eV. Both show $Pt_4/O_4/CeO_2(100)$ is stable.

Model	# of CeO_2/Unit Cell	# of Pt/Unit Cell	# of O/Unit Cell	Total energy (eV)
$Pt_4/O_4/CeO_2(100)$	14	4	4	-383.22
$CeO_2(100)$	14	0	0	-334.94
Pt bulk (Pt_4)	0	4	0	-24.39
PtO bulk (Pt_2O_2)	0	2	2	-23.11
PtO_2 bulk (Pt_2O_4)	0	2	4	-34.94

Estimation on the Pt density on (100) surface of nano ceria for the SAC sample

The Pt density of Pt on (100) of nano ceria could be obtained by using the Equation (1):

$$Surface\ density\ of\ Pt\ on\ (100)\ of\ nano\ ceria = \frac{\frac{W_{Pt}}{M_{Pt}} \cdot N_A}{W_{\text{nano ceria}} \cdot S_{100}} \qquad \text{Eq. (1)}$$

In Equation (1), W_{Pt} ($W_{\text{nano ceria}}$) is the weight of Pt atoms (nano ceria) in the sample. In our SAC sample, there are two types of ceria: 25% of them is nano ceria which supports Pt single atoms and 75% of them is commercial ceria which supports hybrid Pt/ nano CeO_2. The weight loading of Pt (over all ceria) is about 1.8% and then about 7.2% for $W_{Pt}/W_{\text{nano ceria}}$ in Equation (1). M_{Pt} is the molecular weight of Pt and it is 195.084 g/mol. N_A is Avogadro's number. S_{100} is the (100) surface area of nano ceria per unit mass.

We performed the Brunauer−Emmett−Teller (BET) measurements on the as-prepared SAC sample and the obtained surface area of the sample is about 33 m^2/g. For estimation, we assume there is only ceria in the sample: commercial ceria (the surface area is about 33 m^2/g) and nano ceria, and for nano ceria, the dominating surface is (100). Then the surface area of (100) surface in nano ceria is also about 33 m^2/g. By applying 33 m^2/g for S_{100} in Equation (1), the obtained Pt density is 6.6 atoms/nm^2 which is also the Pt density obtained from the model in Figure 6.