

Supplementary Information for
**Three-dimensional atomic interface between metal and oxide in
Zr-ZrO₂ nanoparticles**

Yao Zhang^{1,5}, Zezhou Li^{1,5}, Xing Tong^{2,5}, Zhiheng Xie¹, Siwei Huang¹, Yue-E
Zhang^{2,3}, Hai-Bo Ke^{2*}, Wei-Hua Wang^{2,4}, Jihan Zhou^{1*}

¹*Beijing National Laboratory for Molecular Sciences, Center for Integrated Spectroscopy, College of Chemistry and Molecular Engineering, Peking University; Beijing, 100871, China.*

²*Songshan Lake Materials Laboratory, Dongguan 523808, China.*

³*College of Physics, Liaoning University, Shenyang 110036, China.*

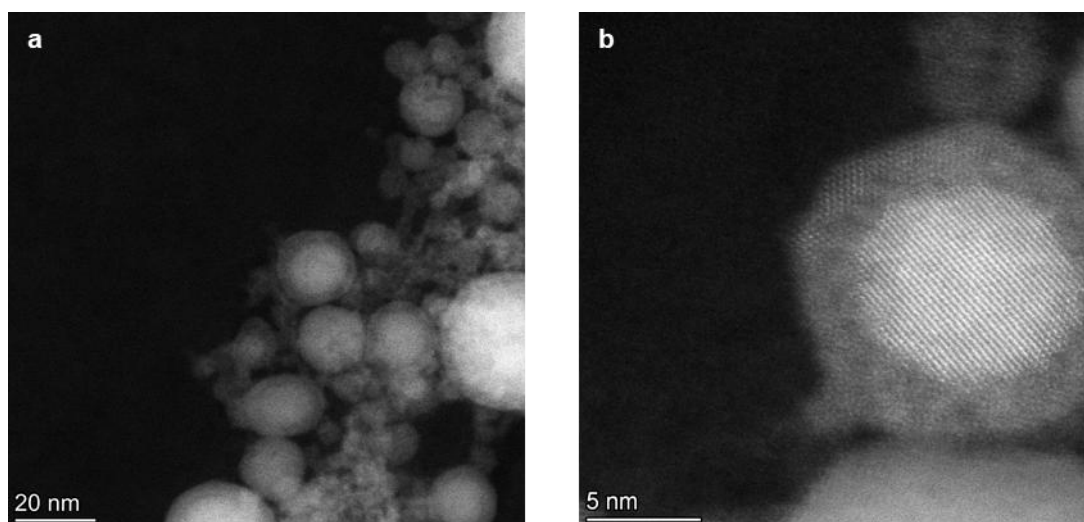
⁴*Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.*

⁵*These authors contributed equally to this work.*

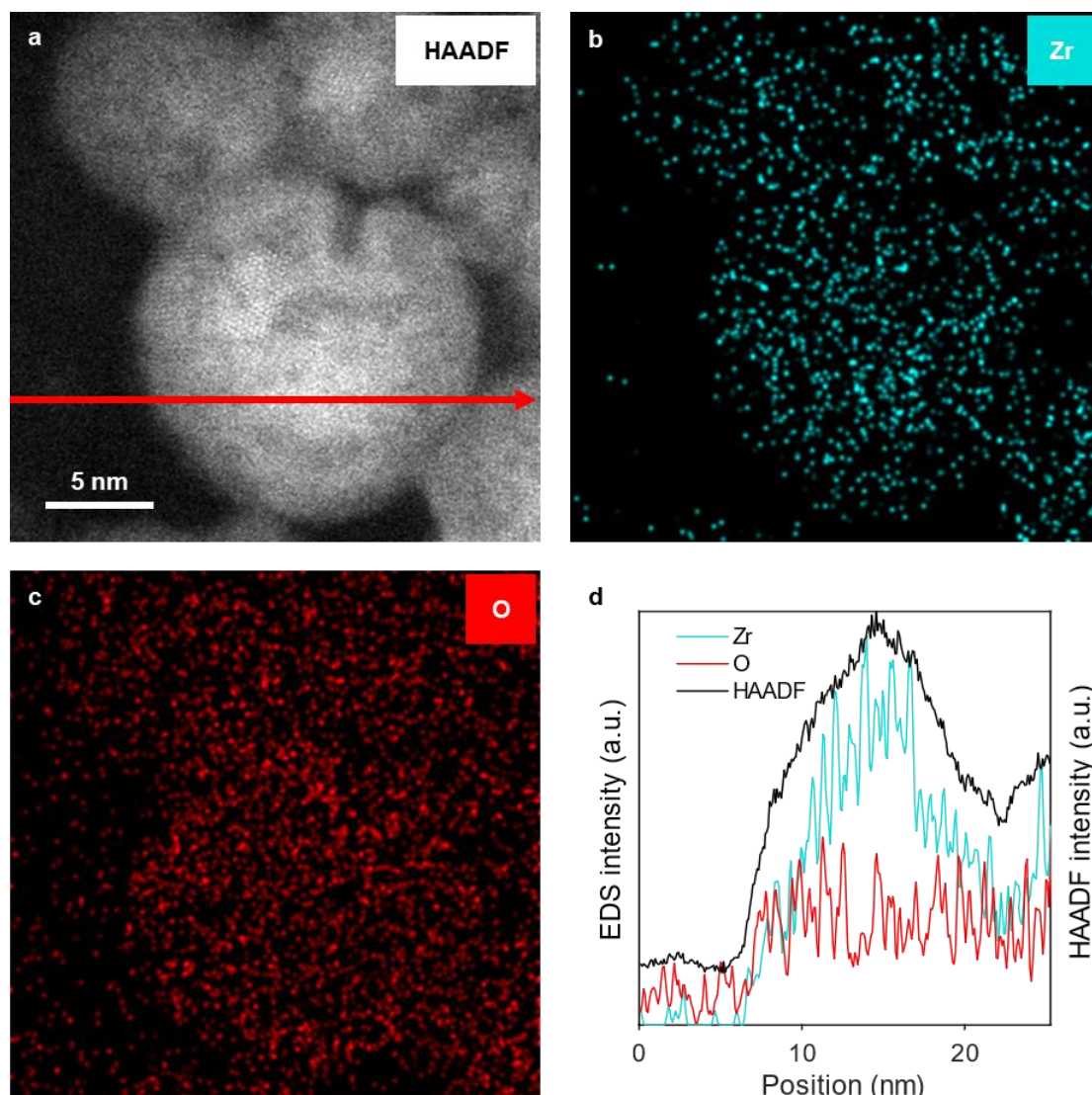
**Correspondence and requests for materials should be addressed to H.-B. K. (email: kehaibo@sslabor.org.cn) and J. Z. (email: jhzhou@pku.edu.cn)*

Supplementary Table 1 Tomography and reconstruction overview

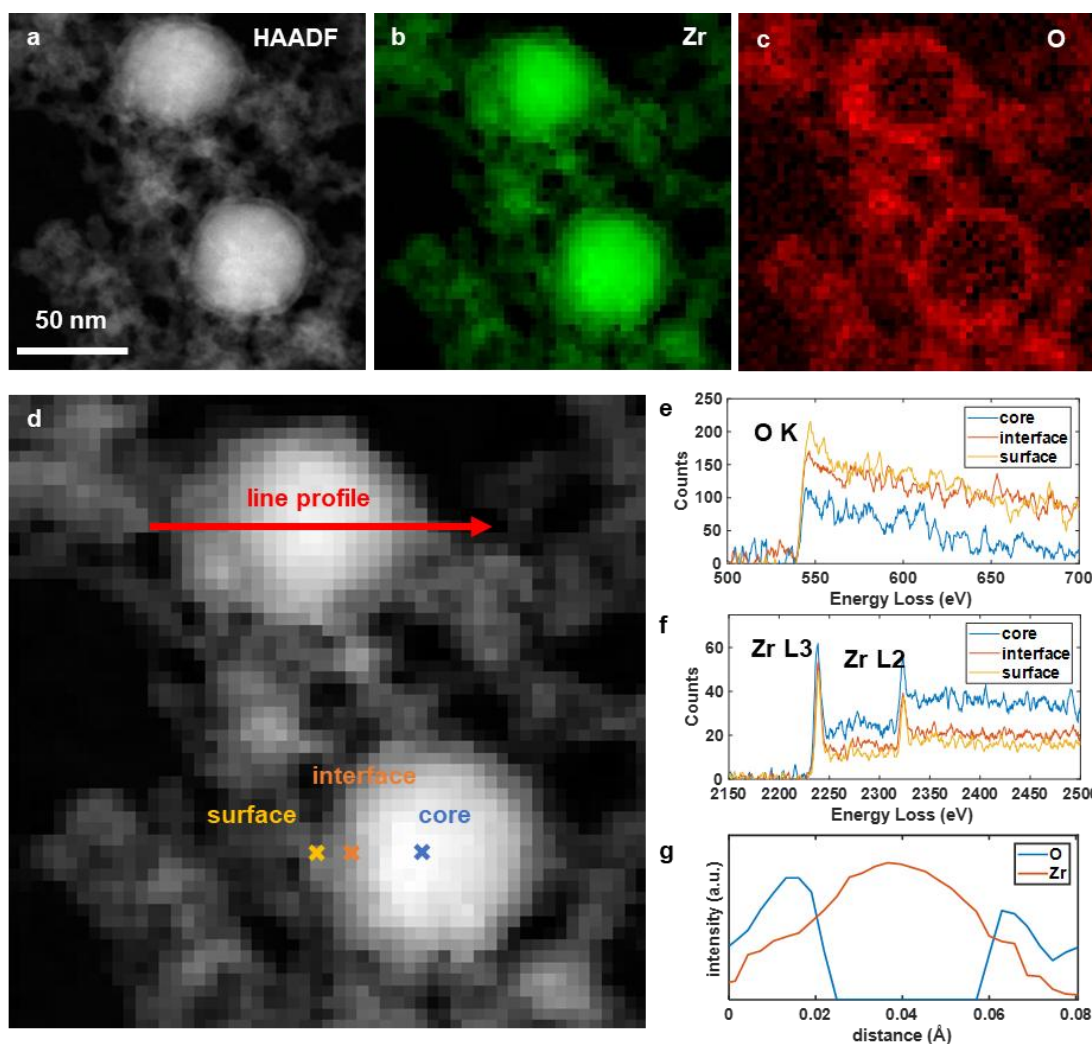
	Zr1	Zr2	Zr3
Data Collection and Processing			
Voltage (kV)	300	300	300
Convergence semi-angle (mrad)	21.4	21.4	21.4
Detector inner angle (mrad)	39.4	31.5	31.5
Detector outer angle (mrad)	200	190.6	190.6
Pixel size (Å)	0.343	0.343	0.343
Scanning current (pA)	15	15	15
Number of projections	50	59	57
Tilt range (°)	-75	-76	-75
	76	77	75.5
Electron dose ($10^5 \text{ e} \cdot \text{Å}^{-2}$)	4.8	3.4	2.9
Reconstruction			
Algorithm	RESIRE		
Oversampling ratio	4	4	4
Number of iterations	200	200	200
Reconstruction error (%)	0.1069	0.0728	0.0990
Number of atoms	15392	22382	13482



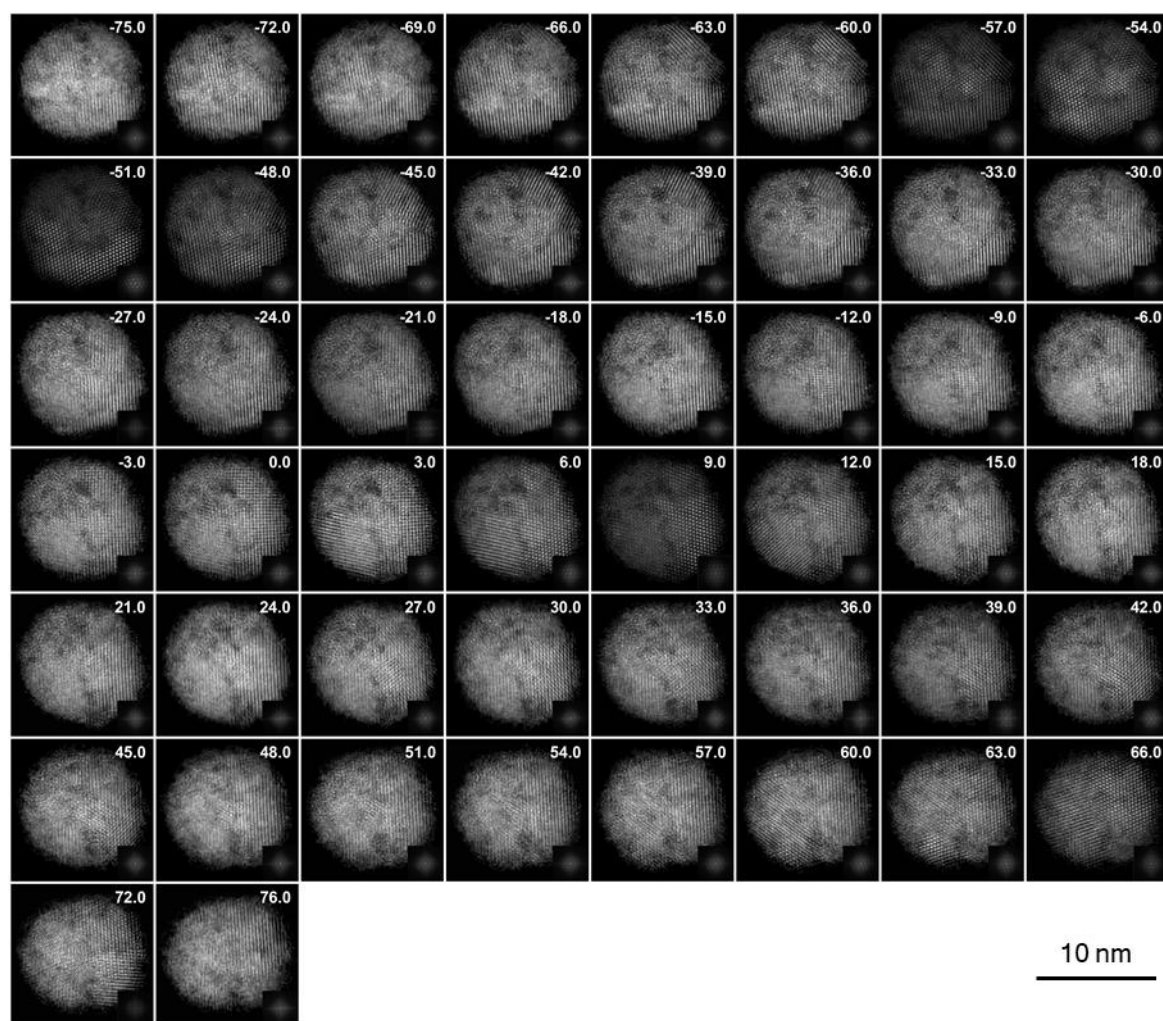
Supplementary Figure 1 HAADF-STEM images show the Zr-ZrO₂ NPs with an oxidized shell and a metal core. **a**, A relatively low magnification image shows overview of the oxidized Zr NPs. **b**, A high-resolution image shows a representative Zr-ZrO₂ NP with a metal core (high intensity) and an oxide shell (low intensity).



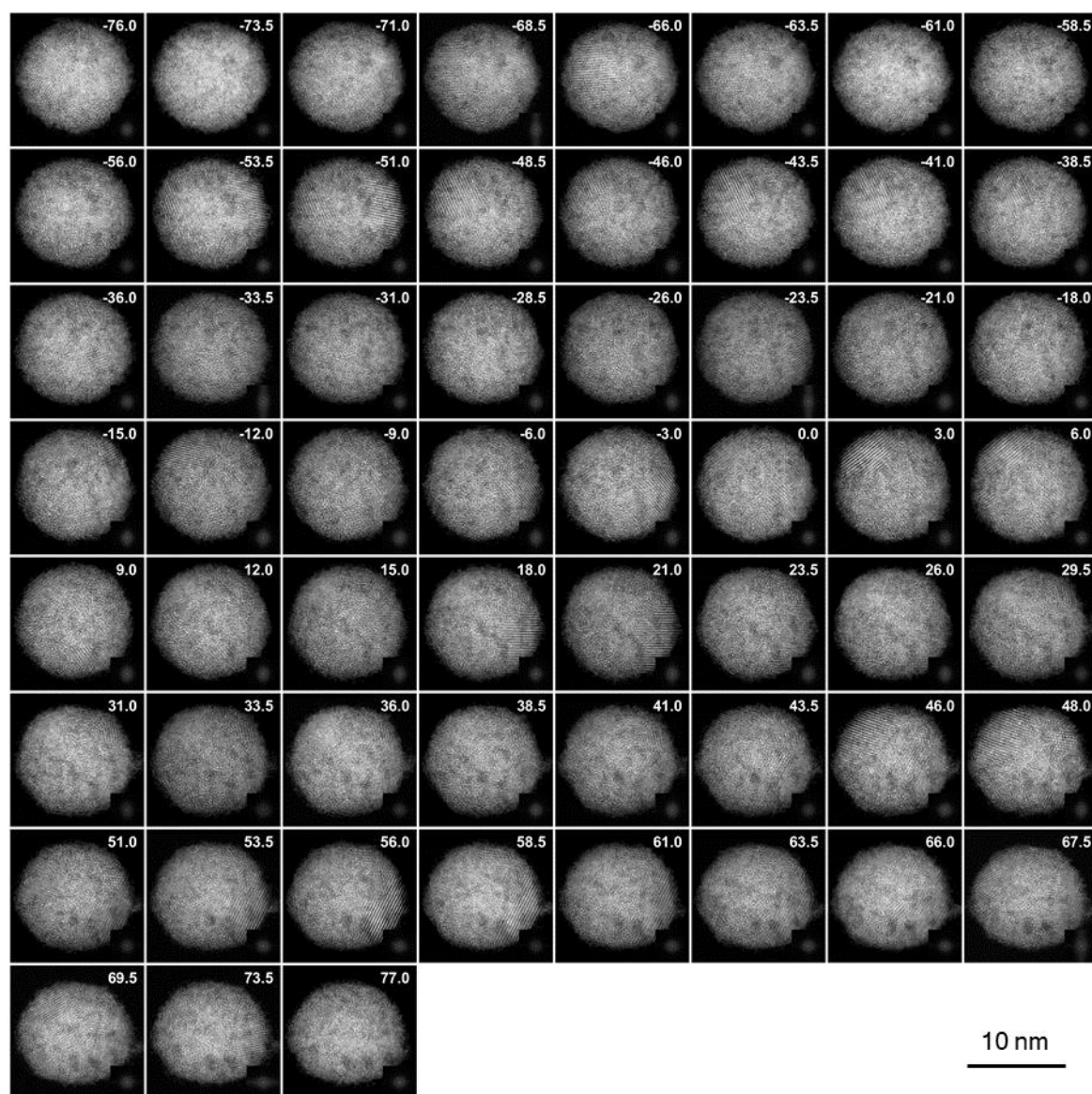
Supplementary Figure 2 EDS mapping and profile show the elements distribution of Zr-ZrO₂ NPs. The HAADF-STEM image (a) and its corresponding Zr (b), O (c) EDS mapping, with high Zr signals and low O signals at the center of the NP confirmed by the line profile (d) along the red arrow in (a).



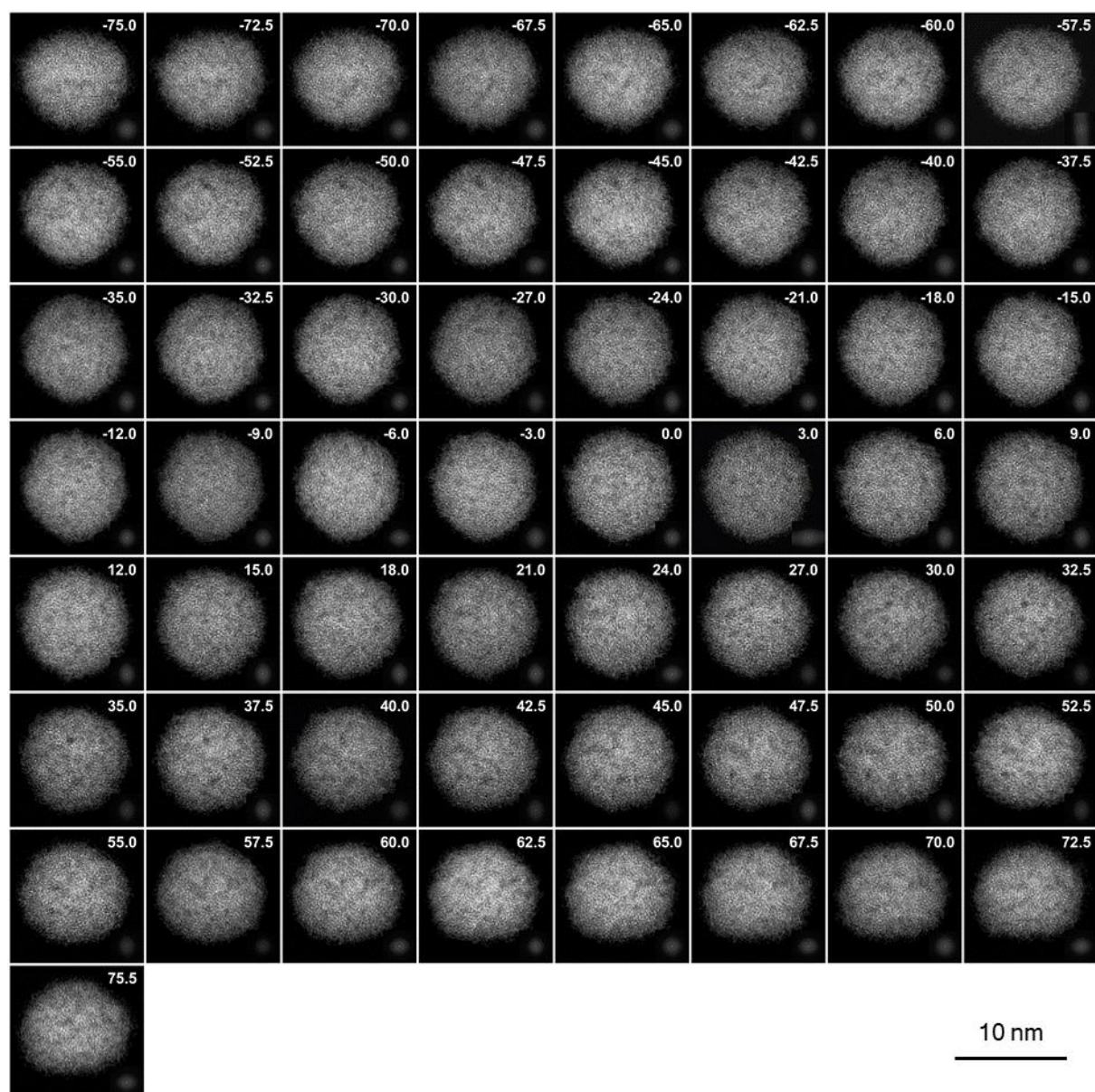
Supplementary Figure 3 EELS mapping shows the elements distribution of Zr-ZrO₂ NPs. The HAADF-STEM image (a) and its corresponding Zr (b), O (c) EELS mapping, with high Zr signals at the center of the NP and high O signals at the edge. The EELS spectra of O (e) and Zr (f) from the points picked in (d) at core (blue), interface (orange) and surface (yellow). (g) The intensity profile of Zr and O respectively along the red arrow in (d).



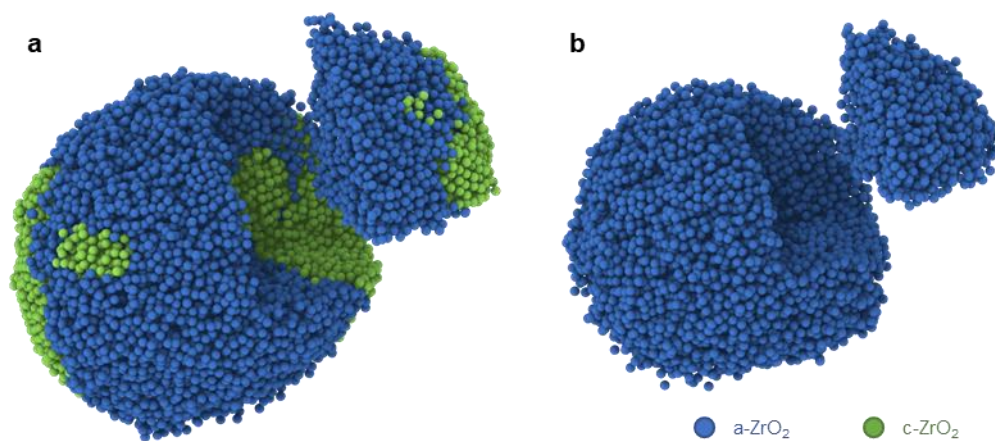
Supplementary Figure 4 Tomography tilt series of the Zr1 NP. 50 HAADF-STEM images with a tilt range from -75.0° to $+76.0^{\circ}$. The Fourier transform of each image is displayed in the bottom-right corner.



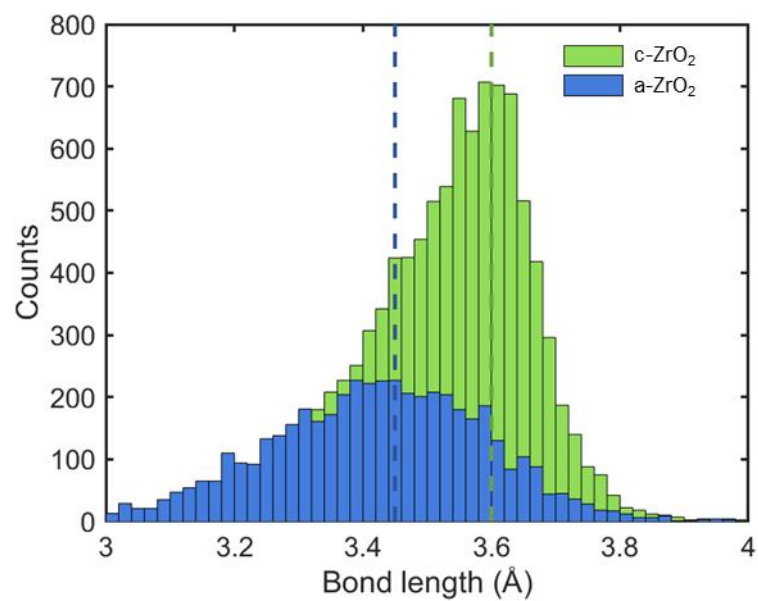
Supplementary Figure 5 Tomography tilt series of the Zr₂ NP. 59 HAADF-STEM images with a tilt range from -76.0° to $+77.0^{\circ}$. The Fourier transform of each image is displayed in the bottom-right corner.



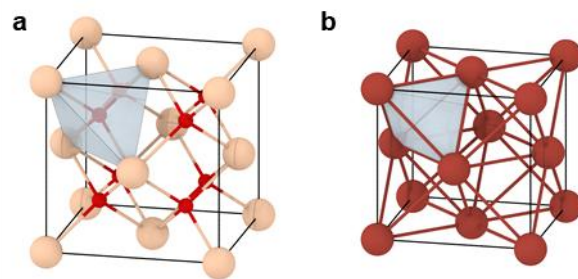
Supplementary Figure 6 Tomography tilt series of the Zr₃ NP. 57 HAADF-STEM images with a tilt range from -75.0° to $+75.5^\circ$. The Fourier transform of each image is displayed in the bottom-right corner.



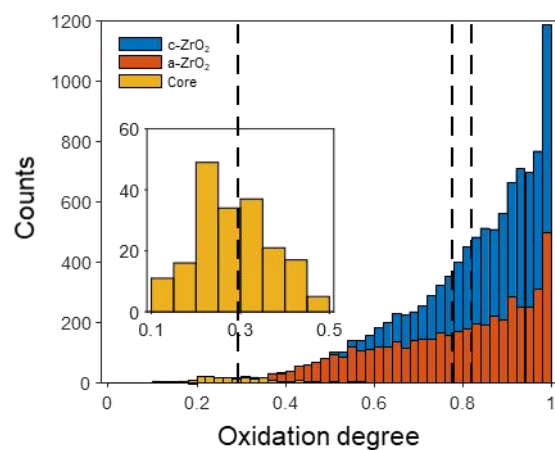
Supplementary Figure 7 Atomic model for Zr2 and Zr3 NPs. **a**, Atomic model for Zr2 NP, with crystalline oxide grains (c-ZrO₂; in green) and a large amorphous oxide phase (a-ZrO₂; in blue). **b**, Atomic model for Zr3 NP, which contains a-ZrO₂ only.



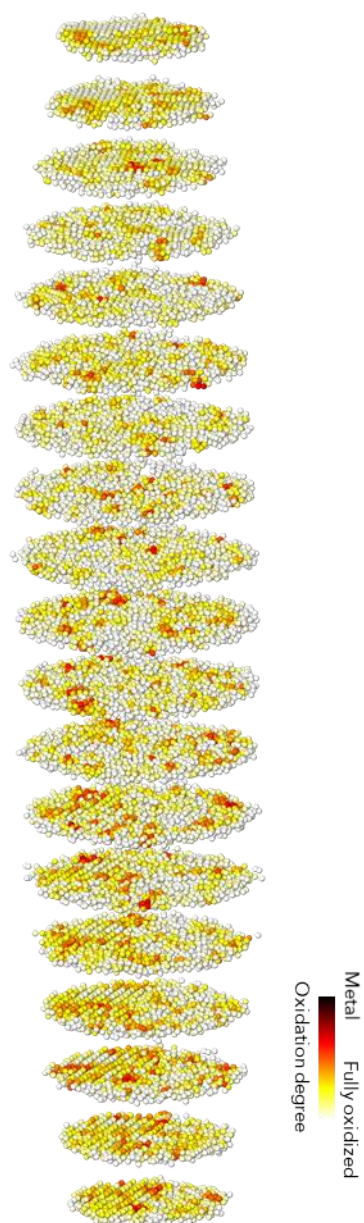
Supplementary Figure 8 Bond length distribution of Zr1 NP, with c-ZrO₂ in green and a-ZrO₂ in blue. The histogram shows the distribution of bond length in c-ZrO₂ and a-ZrO₂. The dashed lines show the most populated bond length in c-ZrO₂ (3.6 Å; the green line) and a-ZrO₂ (3.45 Å; the blue line).



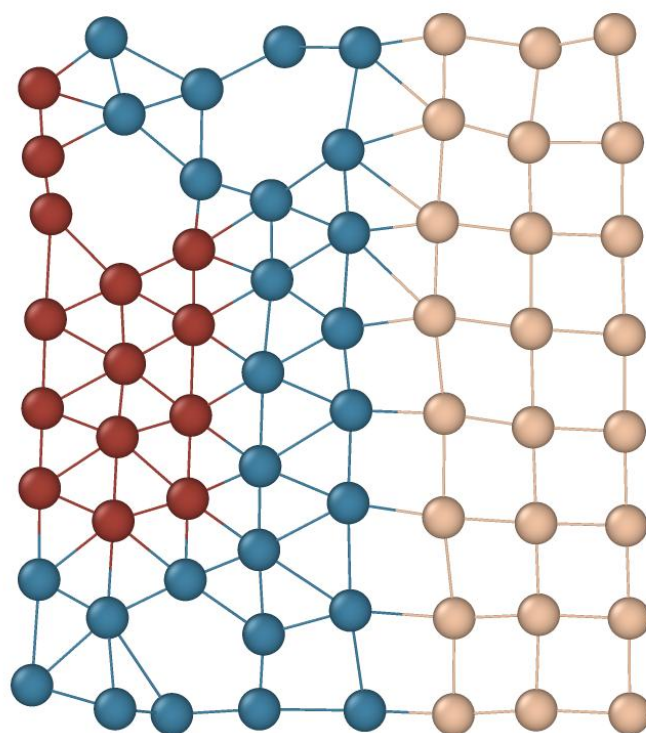
Supplementary Figure 9 The volume difference of the tetrahedral site in pure FCC Zr and c-ZrO₂. **a**, The tetrahedral site in c-ZrO₂, which accommodates one oxygen atom. The atoms in ivory are oxide Zr atoms, and the atoms in red are O atoms. **b**, The tetrahedral site in FCC Zr. The atoms in deep red are metal Zr atoms. Both in **(a)** and **(b)**, the tetrahedron is displayed with surface rendering in light blue.



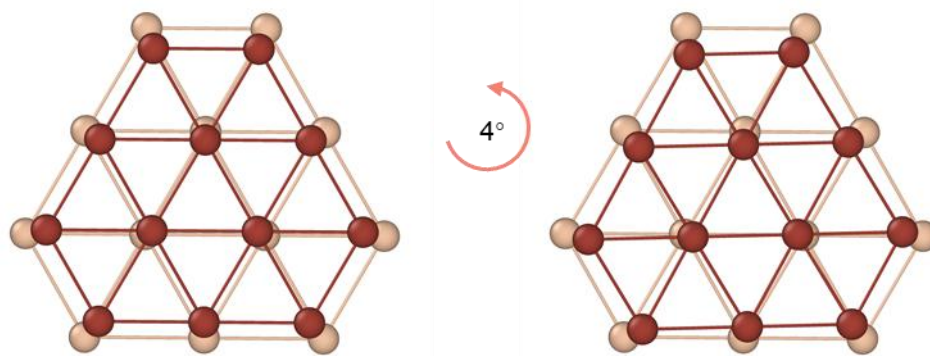
Supplementary Figure 10 The distribution of degree of oxidation. The histogram shows the distribution of degree of oxidation in c-ZrO₂, a-ZrO₂ and metal core. The dashed lines are the mean values of degree of oxidation for c-ZrO₂ (0.82), a-ZrO₂ (0.78) and metal core (0.29) from right to left. The inset figure shows the magnified histogram of metal core.



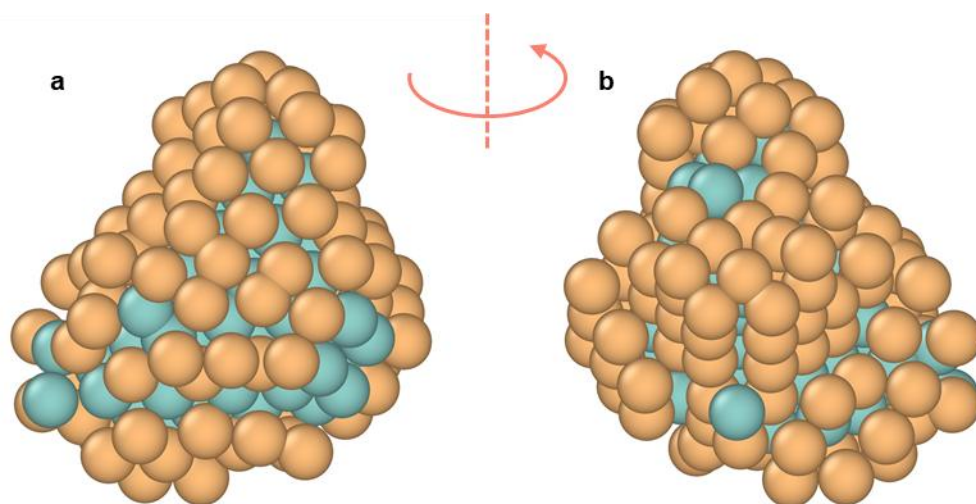
Supplementary Figure 11 Atoms of the Zr₂ NP colored according to the degree of oxidation, divided into slices with a thickness of 5.3 Å. The degree of oxidation shows that the Zr₂ NP is completely oxidized compared with Zr₁ NP.



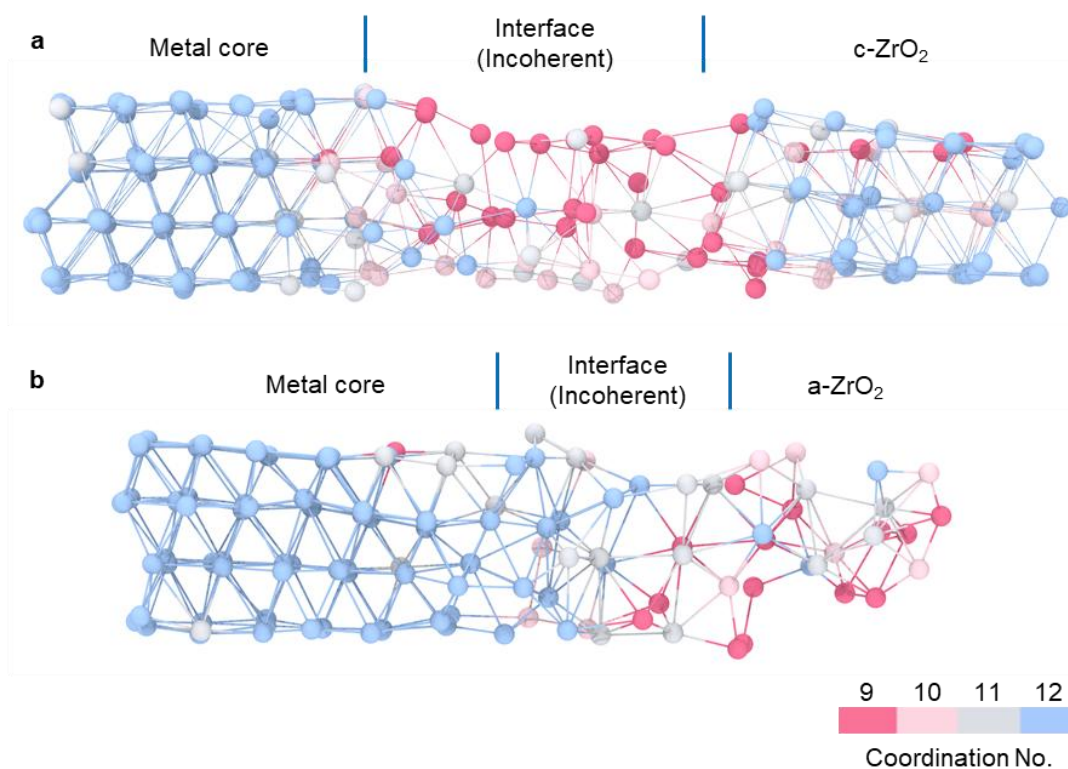
Supplementary Figure 12 The surroundings of the plane in Figure 3g, with the dislocations and vacancies caused by semi-coherent interface. The metal atoms, interfacial atoms and oxide atoms are colored in deep red, blue and ivory, respectively.



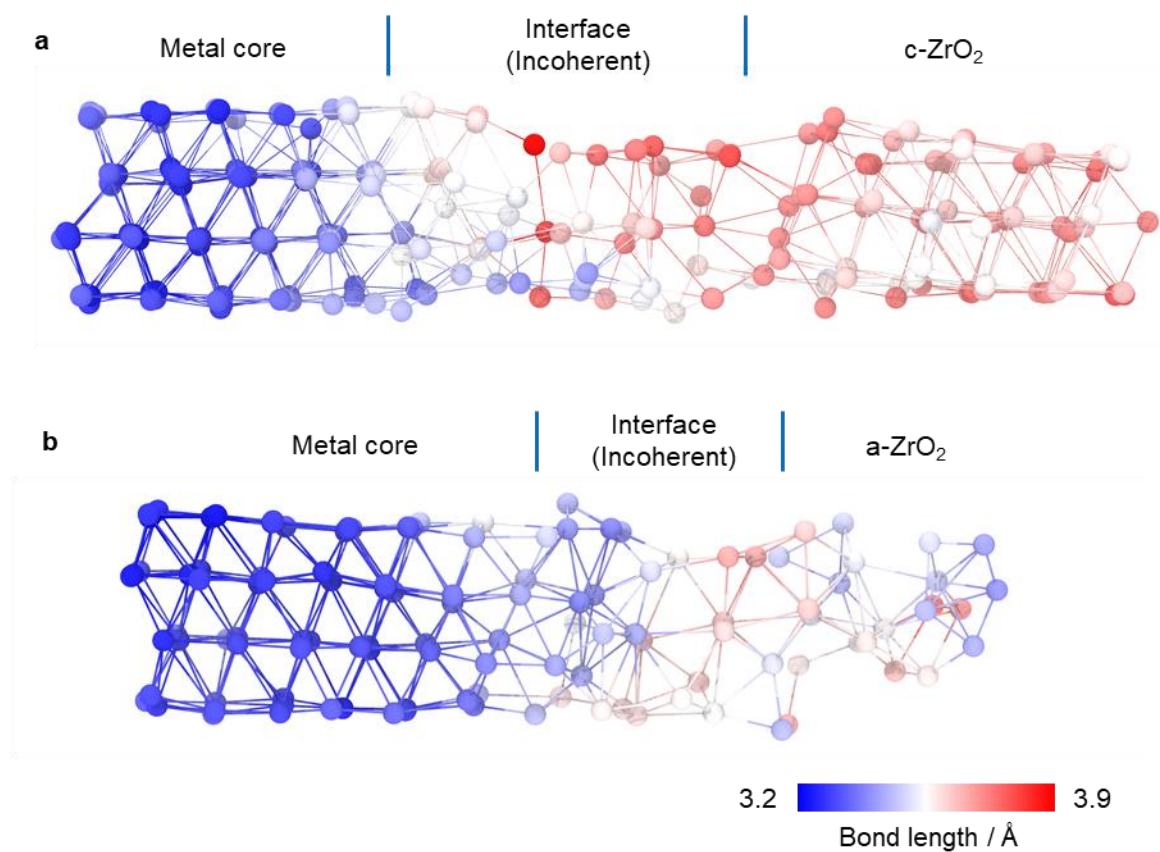
Supplementary Figure 13 The model for the twisting. This figure shows the corresponding {111} planes of metal core and c-ZrO₂ connect with each other. This twisting minimizes the energy of semi-coherent interfaces. The metal Zr atoms and oxide Zr atoms are colored in deep red and ivory, respectively.



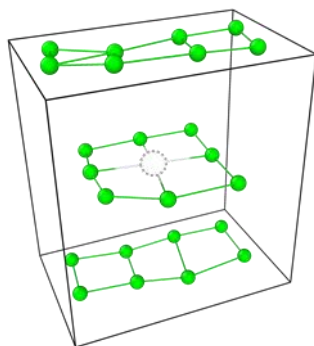
Supplementary Figure 14 All $\{111\}$ faces are colored in orange in metal core, while the other atoms are colored in green. **a**, In the direction of one $\{111\}$ face. **b**, Rotate the metal core to the back.



Supplementary Figure 15 Coordination number of metal/c-ZrO₂ (**a**) and metal/a-ZrO₂ (**b**) incoherent interface. The coordination number is lower at the incoherent interface.



Supplementary Figure 16 Averaged bond length (in Å) of metal/c-ZrO₂ (a) and metal/a-ZrO₂ (b) incoherent interface. The bonds are longer at the incoherent interface.



Supplementary Figure 17 A Zr vacancy displayed with a dashed circle in Zr1 NP. The Zr atoms are colored in green.