Supplementary Information

Probing the atomically diffuse interfaces in core-shell nanoparticles in three dimensions

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This PDF file includes Supplementary Table 1-2 and Supplementary Figs. 1-13.

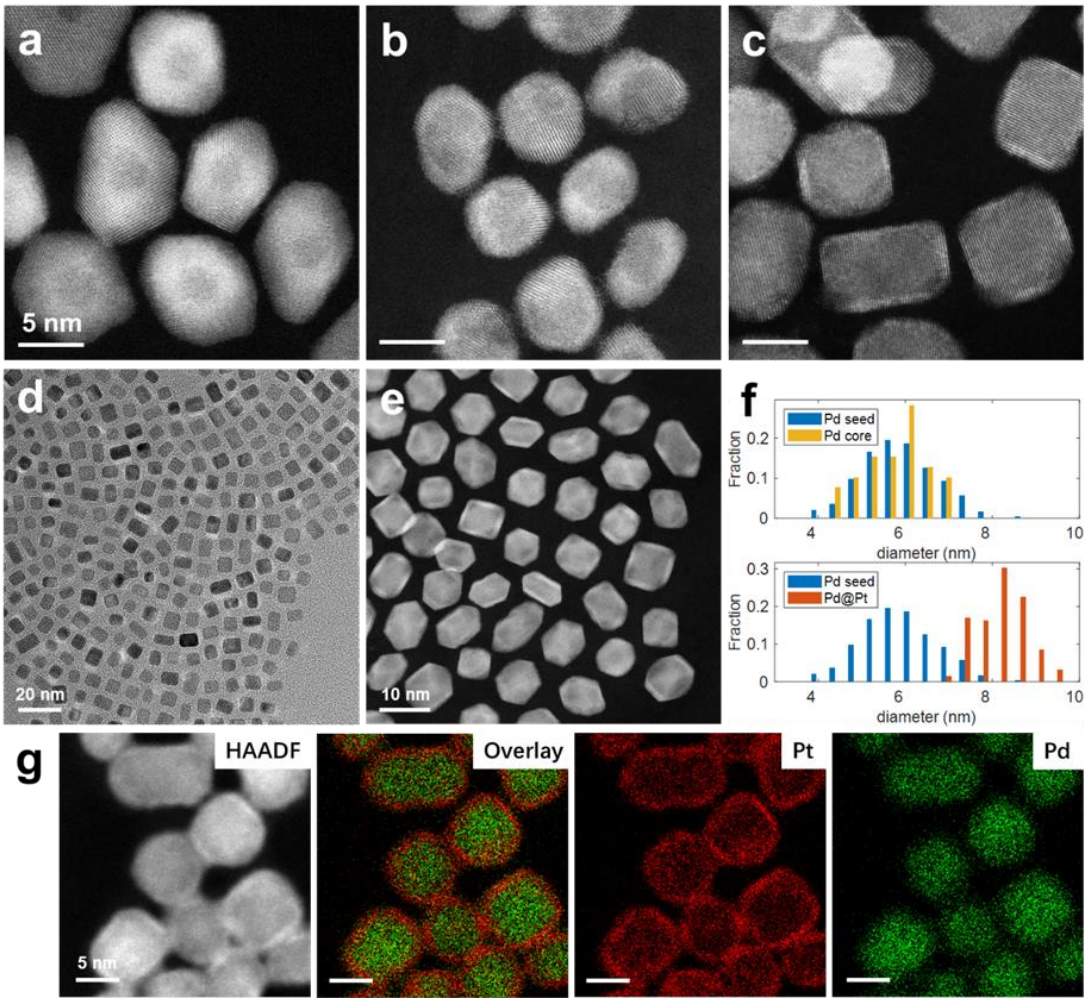
Supplementary Table 1 | Synthesis of Pd@Pt core-shell nanoparticles

	Pd			Pt		
	Precursor	Solvent	Concentration (μmol/ml)	Precursor	Solvent	Concentration (μmol/ml)
PB	$PdAc_2$	oleylamine	1.5	$Pt(acac)_2$		3.3
EPB	$Pd(acac)_2$	oleylamine	2.5	H_2PtCl_6	oleylamine	5.6
TO	Na_2PdCl_4	DI water	1.0	H_2PtCl_6		1.2

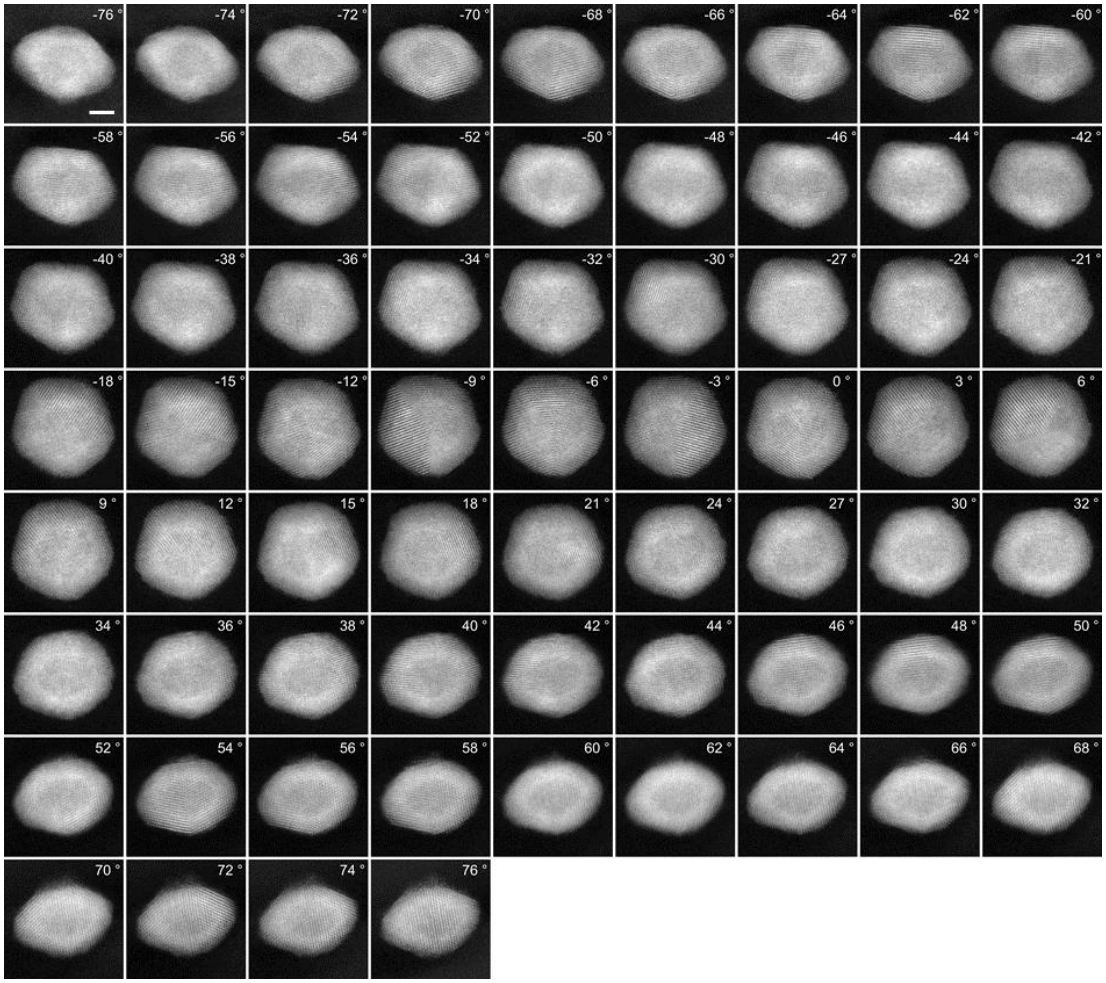
Supplementary Table 2 | Data collection, processing, reconstruction, refinement and statistics

	PB	EPB	TO
Data Collection and Processing			
Voltage (kV)	300	300	300
Convergence semi-angle (mrad)	30.0	30.0	30.0
Probe size (Å)	0.8	0.8	0.8
Detector inner angle (mrad)	39.4	39.4	39.4
Detector outer angle (mrad)	200	200	200
Pixel size (Å)	0.343	0.343	0.343
Number of projections	67	59	60
Tilt range (°)	-76.0	-76.0	-75.5
	76.0	77.0	77.5
Electron dose (10^5 $e^-/Å^2$)	6.4	5.6	5.7
Reconstruction			
Algorithm	RESIRE	RESIRE	RESIRE
Oversampling ratio	4	4	4
Number of iterations	200	200	200
Refinement			
R (%)[a]	4.30	5.66	5.35
Statistics			
# of atoms			
Total	12038	5377	8425
Pd	2054	1372	3649
Pt	9984	4005	4776

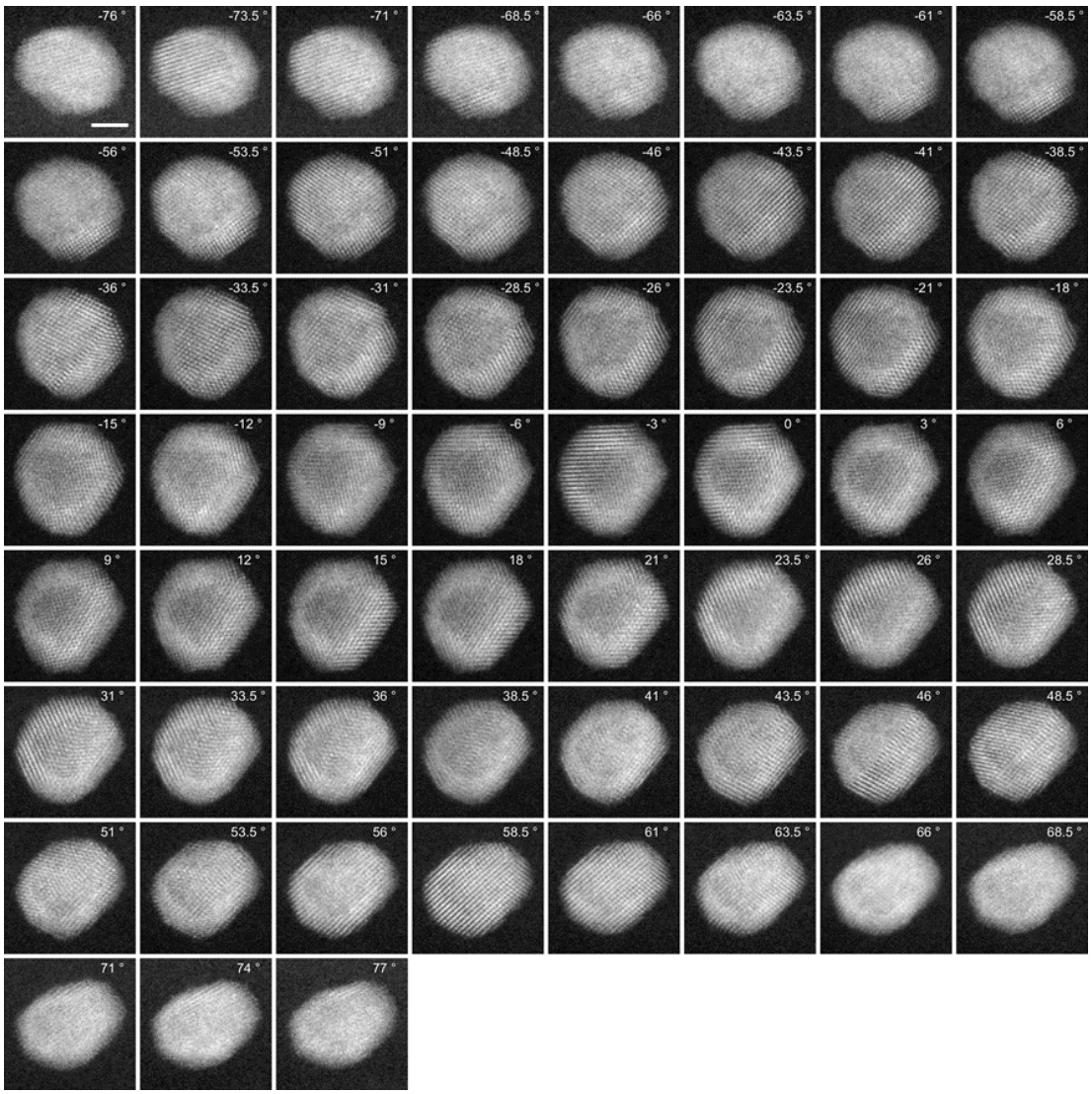
[a] The R-factor is defined by $R = \frac{1}{N}\sum_\theta \frac{\sum_{x,y}|\Pi_\theta(O)\{x,y\} - b_\theta\{x,y\}|}{\sum_{x,y}|b_\theta\{x,y\}|}$, where $\Pi_\theta(O)\{x,y\}$ is the back projection of the reconstruction volume at angle θ, $b_\theta\{x,y\}$ is the real projection image at angle θ, and N is the number of projections.



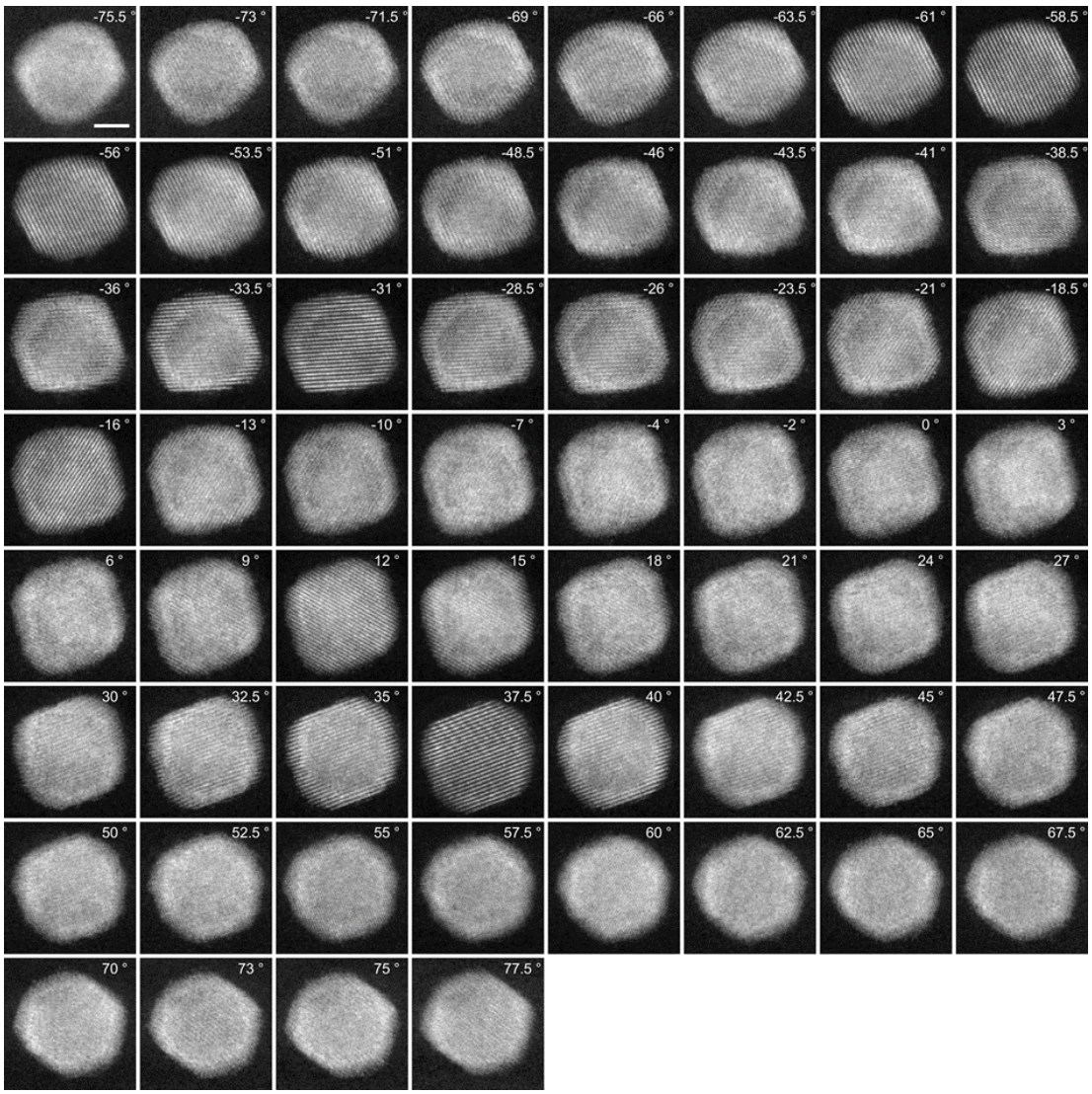
Supplementary Fig. 1 | Characterization of Pd@Pt core-shell nanoparticles synthesized using a two-step chemical reduction procedure. a-c, HAADF-STEM images of PB (**a**), EPB (**b**) and TO (**c**) particles, respectively. **d**, Large scale TEM image of cuboid Pd seed. **e**, Large scale HAADF-STEM image of TO structured Pd@Pt CS-NPs synthesized with Pd seeds in **d**. **f**, Particle size statistics: while the size of Pd seeds is significantly smaller than that of Pd@Pt CS-NPs, the size distribution of both the Pd seeds and the Pd core in Pd@Pt CS-NPs are almost identical. **g**, EDX mapping of Pd@Pt CS-NPs showing well-defined core-shell structure at nanometer scale.



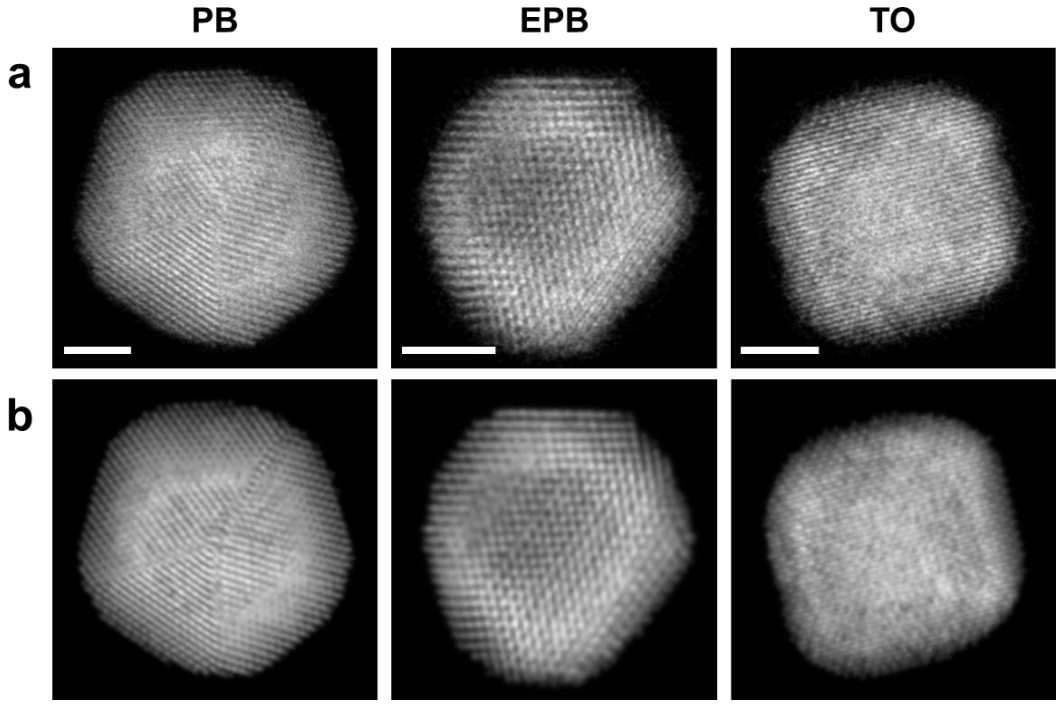
Supplementary Fig. 2 | Tomographic tilt series of PB particle. 67 ADF-STEM images with a tilt range from −76.0° to +76.0°. Scale bar, 2 nm.



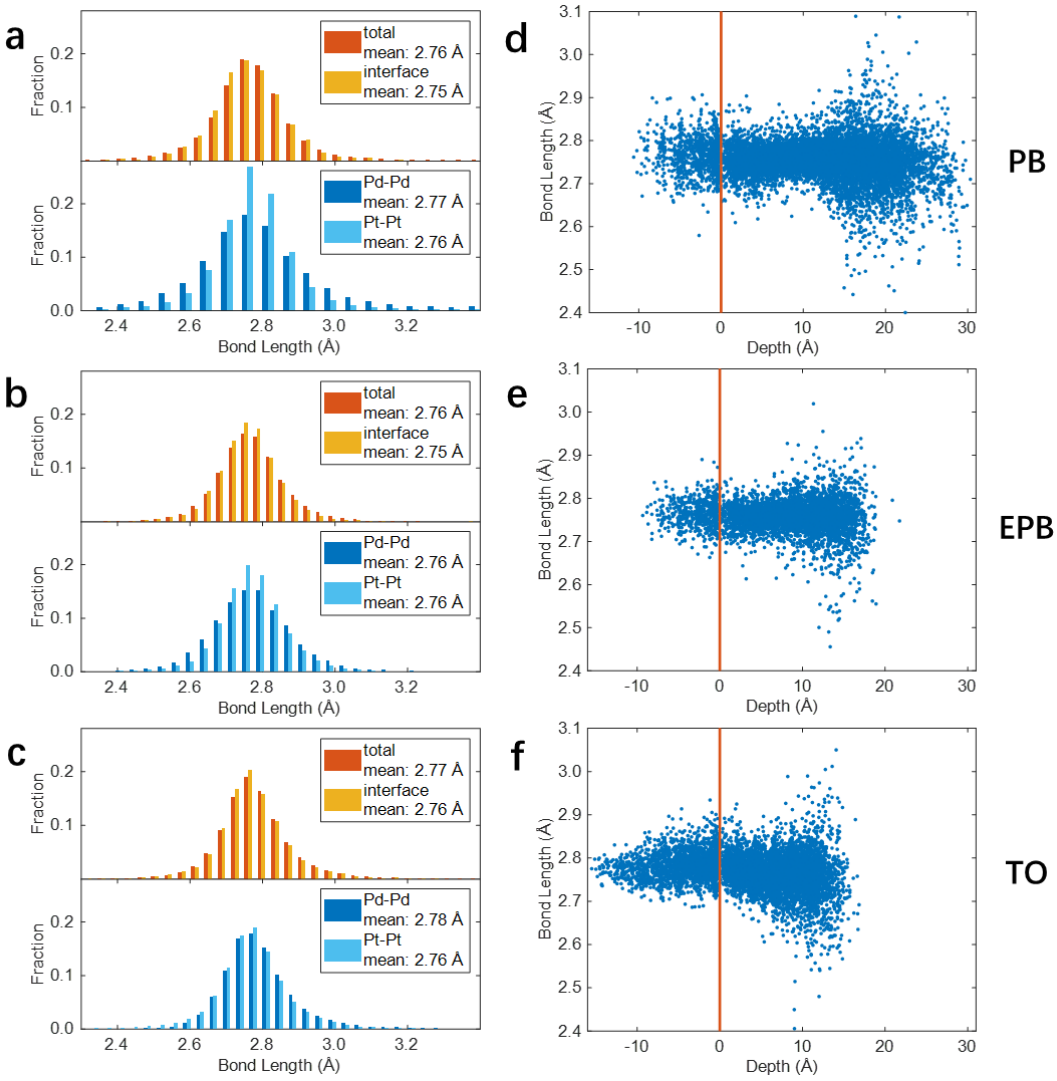
Supplementary Fig. 3 | Tomographic tilt series of EPB particle. 59 ADF-STEM images with a tilt range from −76.0° to +77.0°. Scale bar, 2 nm.



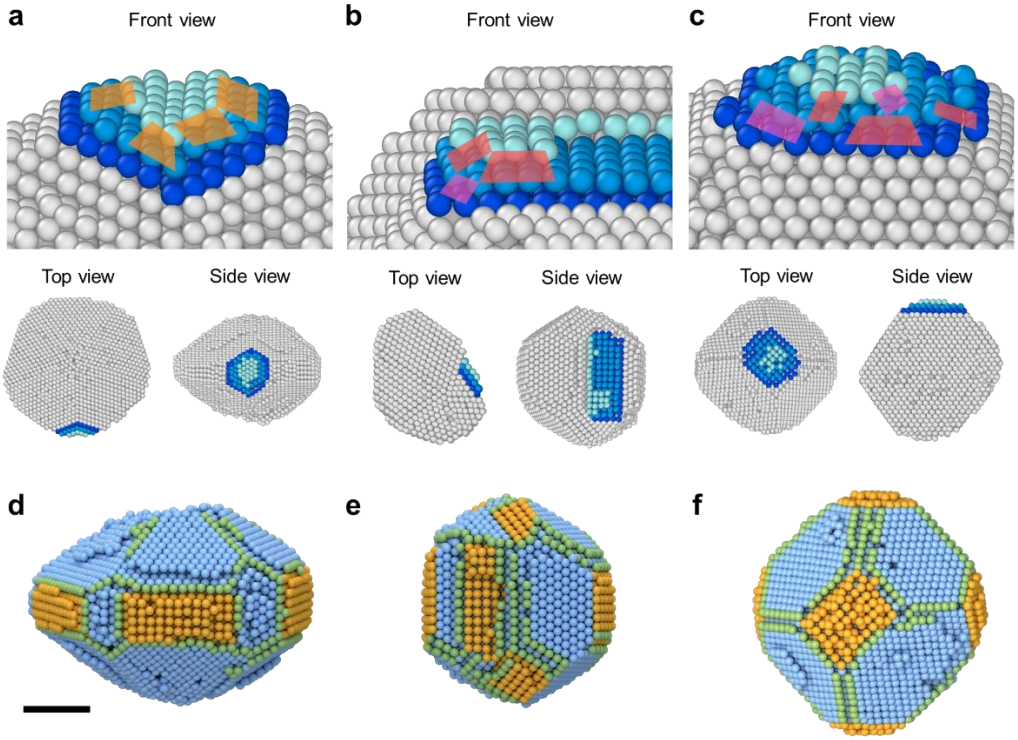
Supplementary Fig. 4 | Tomographic tilt series of TO particle. 60 ADF-STEM images with a tilt range from −75.5° to +77.5°. Scale bar, 2 nm.



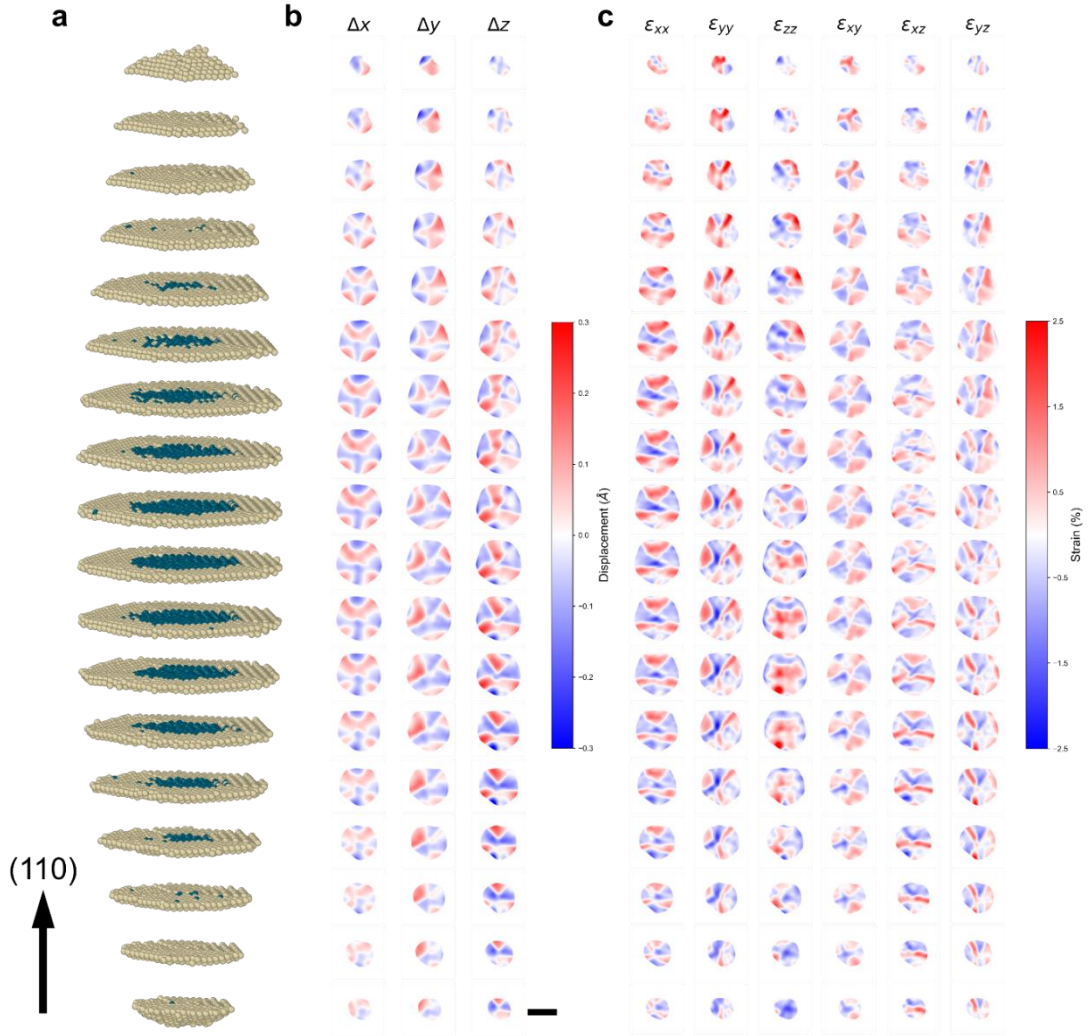
Supplementary Fig. 5 | Consistency check of three nanoparticles. a, ADF-STEM images taken at 0° during tilting experiment for PB, EPB and TO particles. **b**, Simulated forward projections from the final 3D atomic model at the tilt angles giving the best consistency. The best consistent Euler angles were determined as φ: 0°, θ: -0.1°, ψ: -0.4° (PB); φ: -0.2°, θ: -0.1°, ψ: 0.2° (EPB); φ: -0.1°, θ: 0.9°, ψ: -0.5° (TO), respectively. Scale bar, 2 nm.



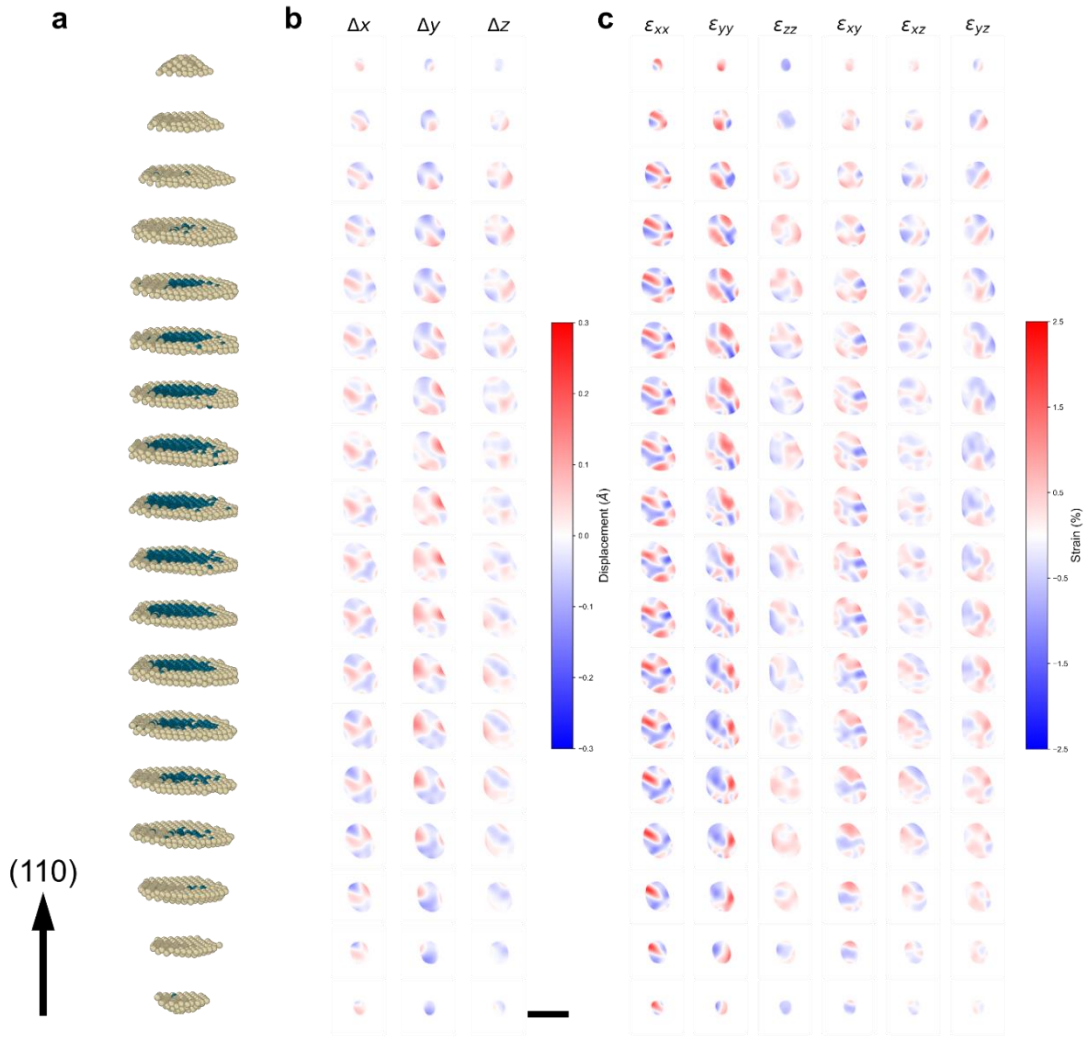
Supplementary Fig. 6 | Bond length statistics of three particles. a-c, Total and interfacial Pd-Pd and Pt-Pt bond length distribution in PB (**a**), EPB (**b**) and TO (**c**) particles. **e-f**, Distribution of bond length versus depth in the particles. Zero depth (red line) is defined at the depth where the mean Pd concentration is ~50 % in each particle.



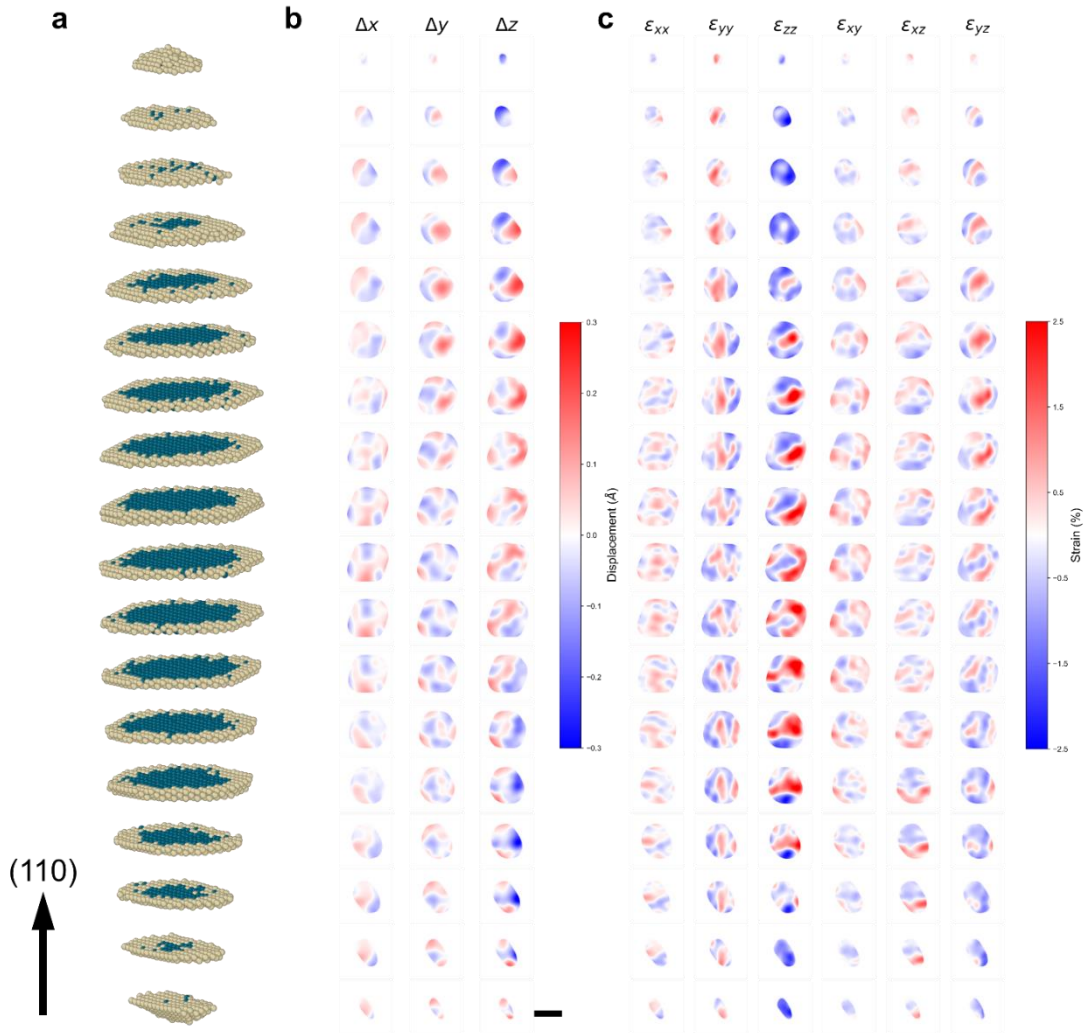
Supplementary Fig. 7 | Complex surface structure of three particles. a-c, Front, top and side view of PB (**a**), EPB (**b**) and TO (**c**) particles, respectively. Pale cyan, blue and indigo color correspond to the first, second and third layer. For PB (**a**) two connected {111} facets are colored. For EPB (**b**) and TO (**c**) the {100} facets is colored. Orange, magenta and red patches represent (S)-[2(111)×(110)], (S)-[2(100)×(100)], (S)-[2(100)×(110)] steps, respectively. **d-f**, 3D Atomic models of EPB (**d**), PB (**e**) and TO (**f**) particles, respectively. Yellow atoms belong to {100} facets, blue atoms belong to {111}, and green atoms represent ridges and edges on the surface. Scale bar for **d-f**, 2nm.



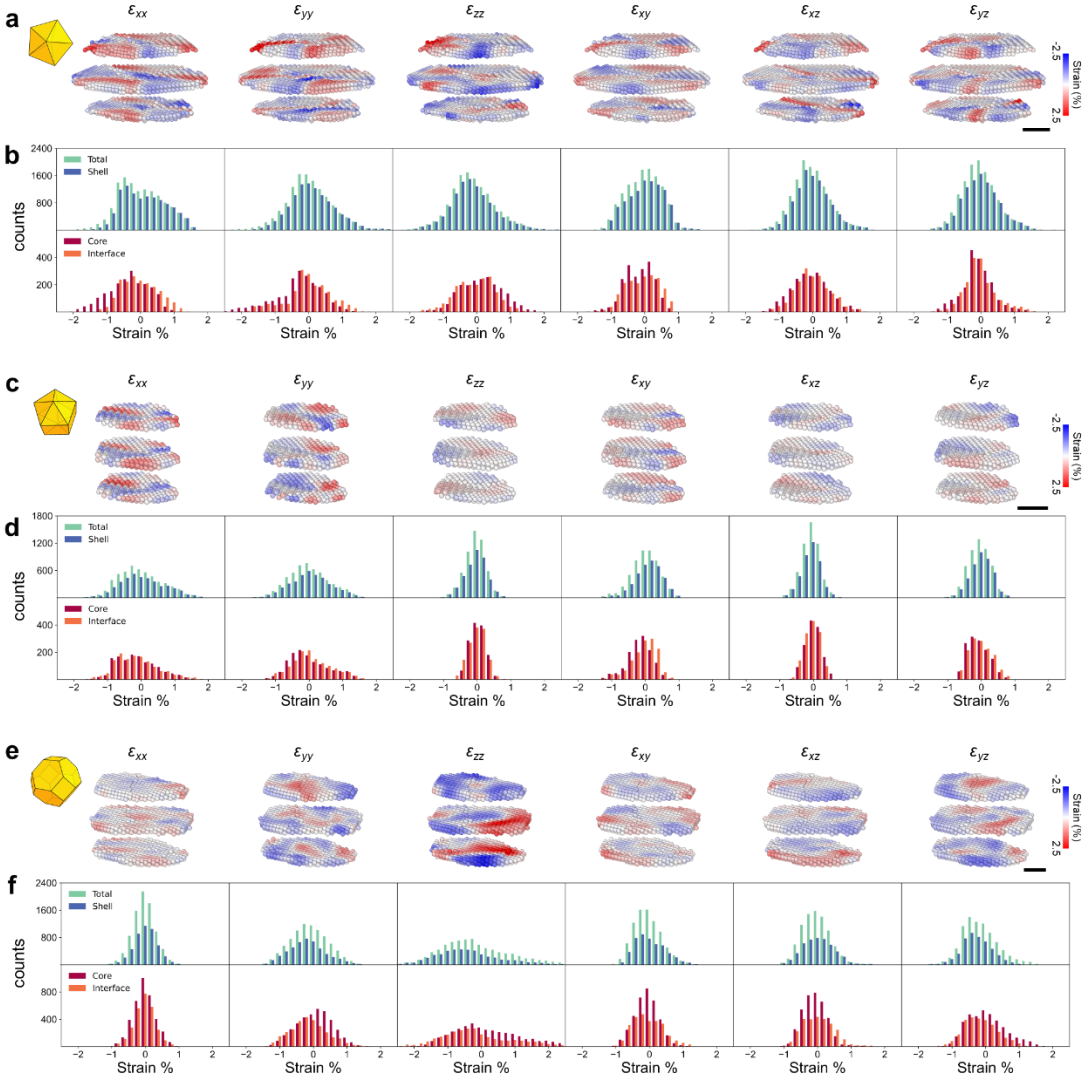
Supplementary Fig. 8 | 3D atomic displacements and strain maps of particle PB. Atomic slices (**a**), 3D displacement field (**b**) and six components of the full strain tensor (**c**) of PB particle. Scale bar for **b** and **c**, 5 nm.



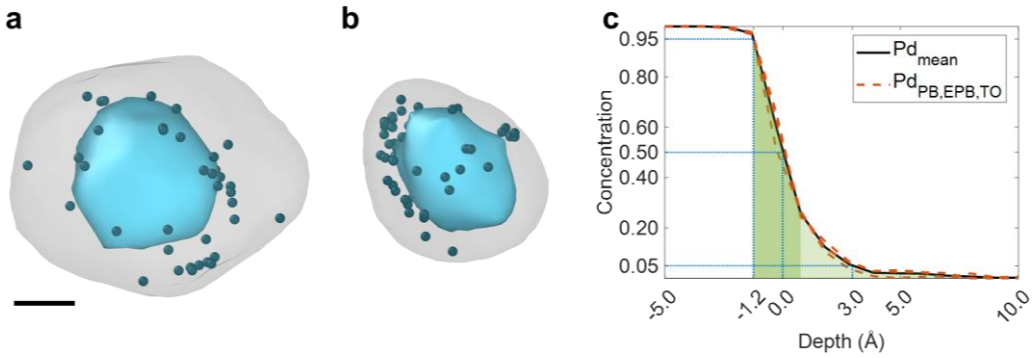
Supplementary Fig. 9 | 3D atomic displacements and strain maps of particle EPB. Atomic slices (**a**), 3D displacement field (**b**) and six components of the full strain tensor (**c**) of EPB particle. Scale bar for **b** and **c**, 5 nm.



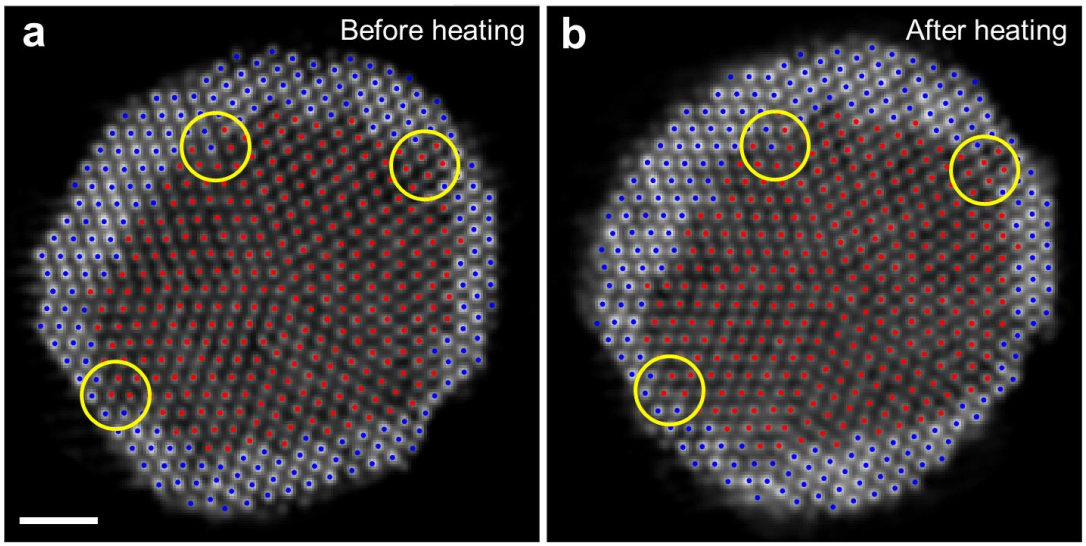
Supplementary Fig. 10 | 3D atomic displacements and strain maps of particle TO. Atomic slices (**a**), 3D displacement field (**b**) and six components of the full strain tensor (**c**) of TO particle. Scale bar for **b** and **c**, 5 nm.



Supplementary Fig. 11 | 3D strain tensor analysis of three particles. a, Sliced maps of the six components of the full strain tensor for PB particle. **b**, Statistics of the strain tensors for total and shell atoms (top), core and core-shell interface atoms (bottom) of PB particle. **c**, Sliced maps of the six components of the full strain tensor for EPB particle. **d**, Statistics of the strain tensors for total and shell atoms (top), core and core-shell interface atoms (bottom) of EPB particle. **e**, Sliced maps of the six components of the full strain tensor for TO particle. **f**, Statistics of the strain tensors for total and shell atoms (top), core and core-shell interface atoms (bottom) of TO particle. Atomic slices in **a** and **c** are perpendicular to the five-fold co-axis along <110> direction. Slices in **e** are also along (110) crystal plane. In **a**, **c** and **e**, strain is indicated by the color scale, and the scale bar is 2 nm.



Supplementary Fig. 12 | Concentration and distribution of Pd in three particles. a-b, Distribution of isolated Pd atoms in PB (**a**) and EPB (**b**) particles, respectively. **c**, Radially-averaged Pd concentrations along the core to the shell for three particles, where the diffuse interface is highlighted with green and pale green bands. The green band represent the area where Pd concentration drops fast from the core to the shell. The pale green band represent the area where Pd concentration decreases slowly. Most of isolated Pd atoms distribute in the pale green area. We chose the depth where Pd concentration equals to 95% and 5% as the range of diffuse interfaces. Zero depth was defined as where Pd concentration equals to 50%. Scale bar for **a-b** is 2 nm.



Supplementary Fig. 13 | The influence of long time heating procedure on the atomically diffuse interfaces. a-b, The same atomic layer of a Pd@Pt CS-NP before (**a**) and after (**b**) heating in the vacuum at 180 ℃ for 48 hrs, obtained from the two independent measurements. Yellow circles highlight consistent diffuse interface areas. The two independent tomographic tilt series were acquired from the same nanoparticle before and after long term baking at 180 ℃. The 3D atomic models from the two measurements were obtained using the same reconstruction, atom tracing, atom identification and refinement procedures. Although some of the surface atoms in the two models are inconsistent due to the surface atom rearrangement during heating and experimental error, the internal atoms belonging to the interface are almost identical. Scale bar for **a-b** is 1 nm.