Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary information

1. X-ray diffraction data and modelling

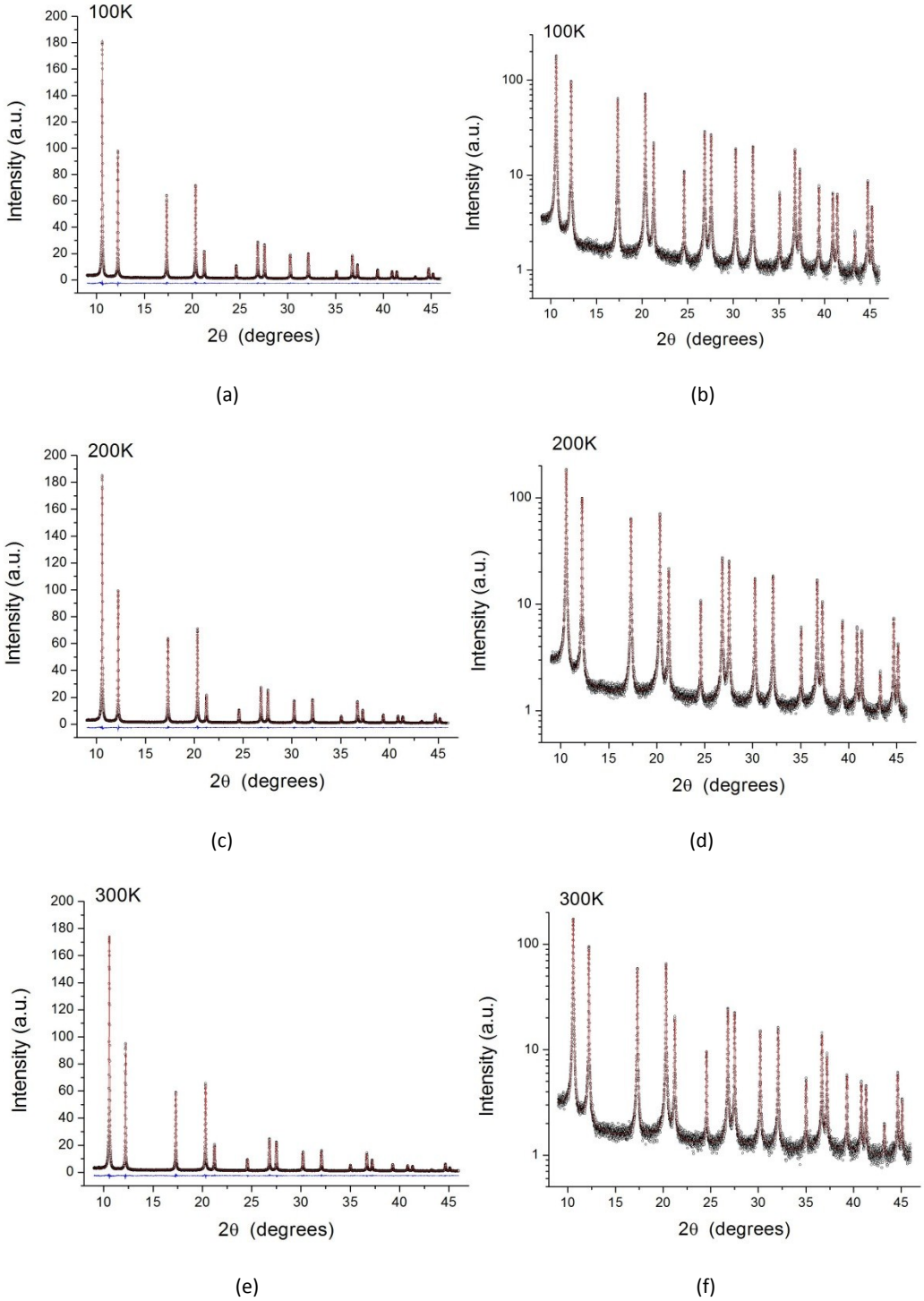


Fig S1: Whole Powder Pattern Modelling of XRPD data: (a), (c) and (e) show data (circle) and modelling (line) with their difference (residual, line below) for the truncated cubes at 100 K, 200 K and 300 K respectively (reproduced with permission from Flor et al. (2018); while (b), (d) and (f) show the corresponding data, with X-axis in a log scale

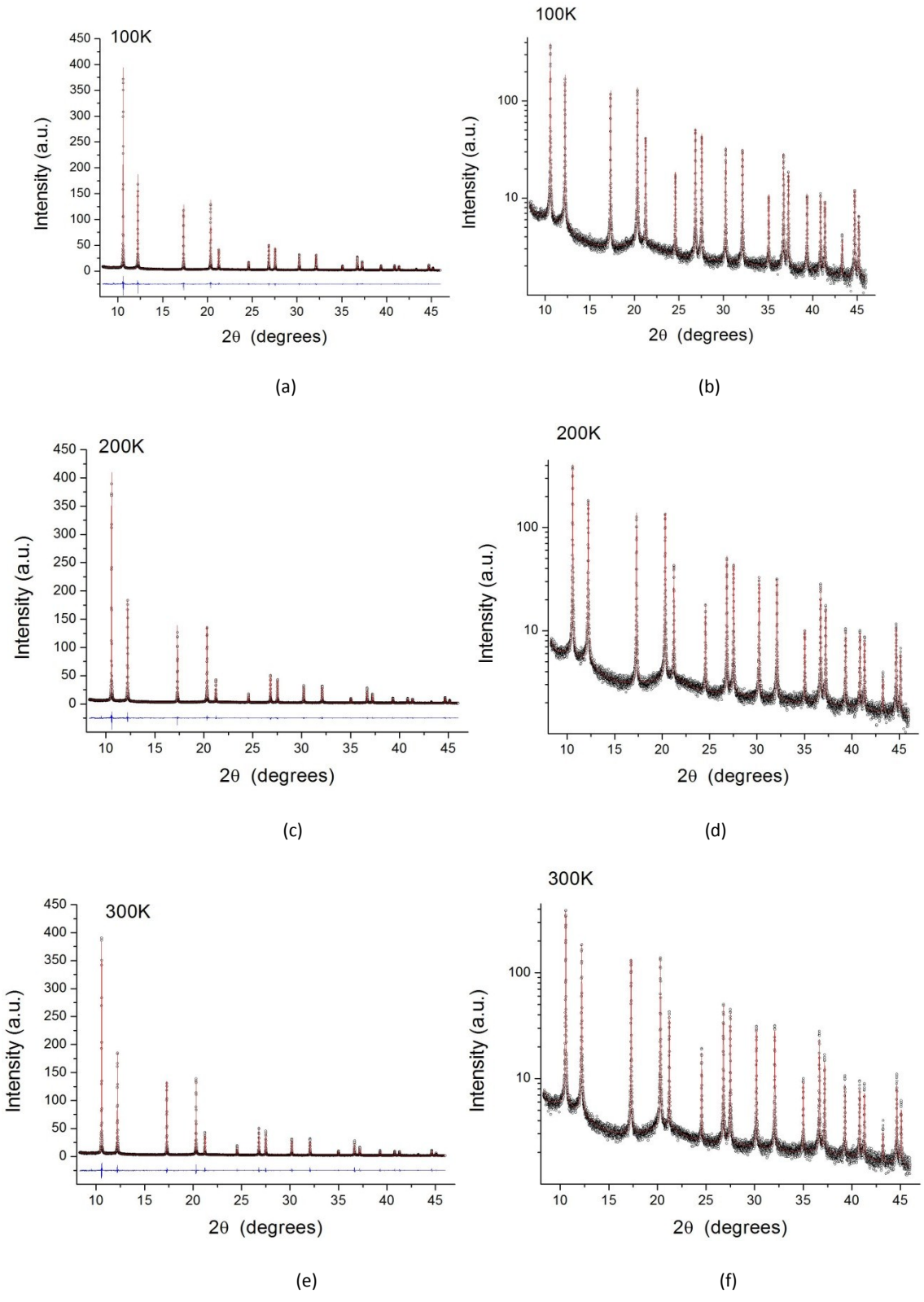


Fig S2: Whole Powder Pattern Modelling of XRPD data: (a), (c) and (e) show data (circle) and modelling (line) with their difference (residual, line below) for the octahedra at 100 K, 200 K and 300 K respectively; while (b), (d) and (f) show the corresponding data, with X-axis in a log scale

3. Variation in lattice parameter

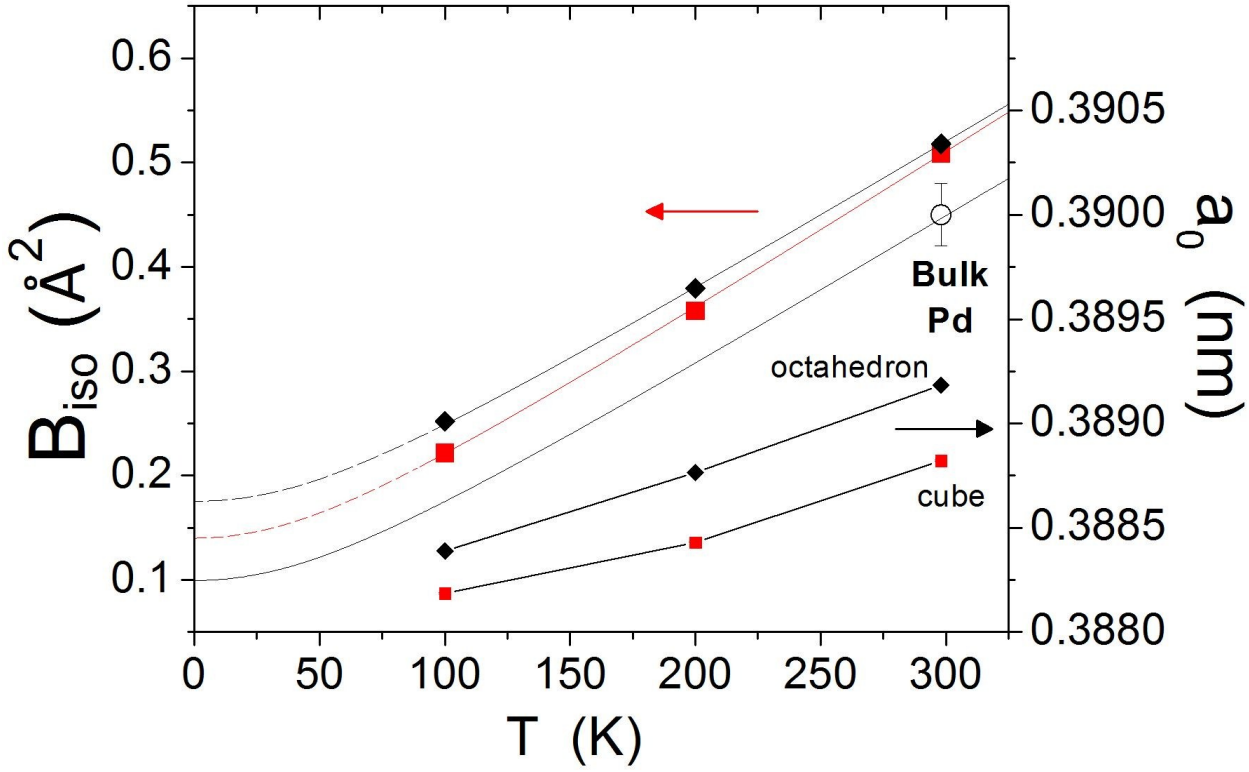
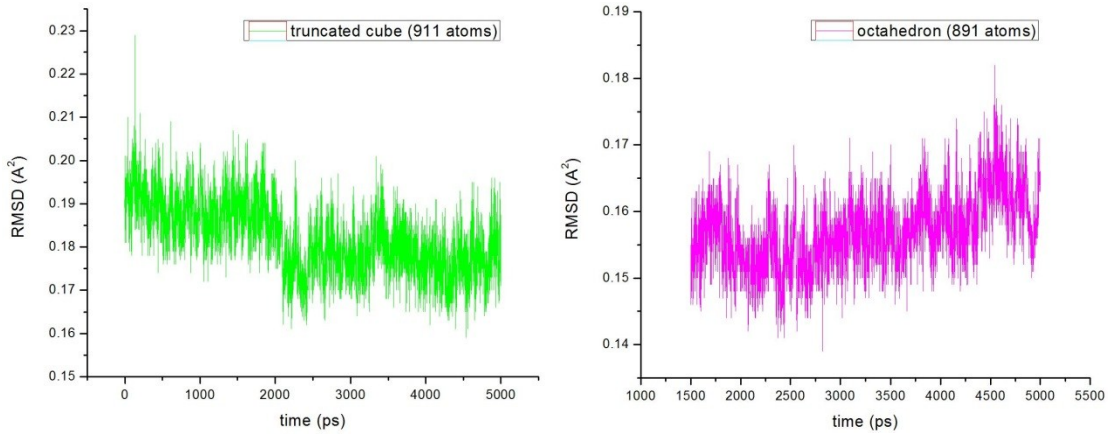


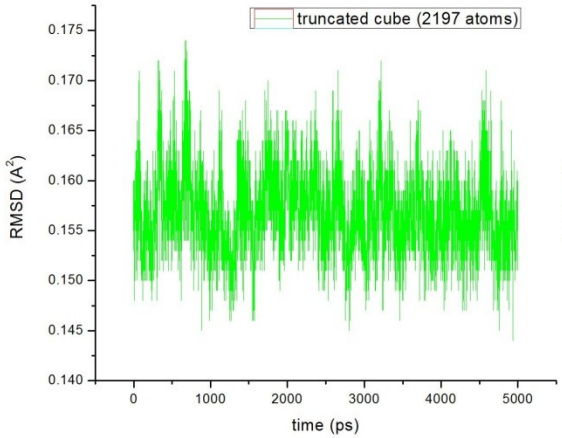
Fig S3. Variation in Debye-Waller factor (B_{iso}) and unit cell parameter (a_0) with the measurement temperature. The change in B_{iso} (shown by the 3 upper curves) is represented on the left axis, while the change in a_0 (shown by the 2 lower curves) is on the right axis. Black diamonds (♦) for nano-octahedra, and red squares (■) for nanocubes; open circle for B_{iso} of bulk Pd. Trends for B_{iso} refer to a Debye model (see text for details).

Aside from the different values of Biso, we also observe a slightly lower (~ 0.003 Å) lattice parameter for the octahedron compared to the cube. This is likely the result of the higher coordination number of the closely packed 111 surfaces enclosing the octahedron, compared to the 100 surfaces enclosing the cube, which being more tightly bound possibly exert a squeezing effect on the octahedral NPs.

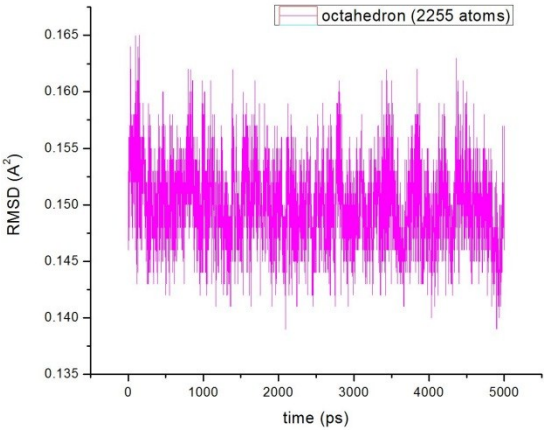
2. Root mean square displacement of simulated particles



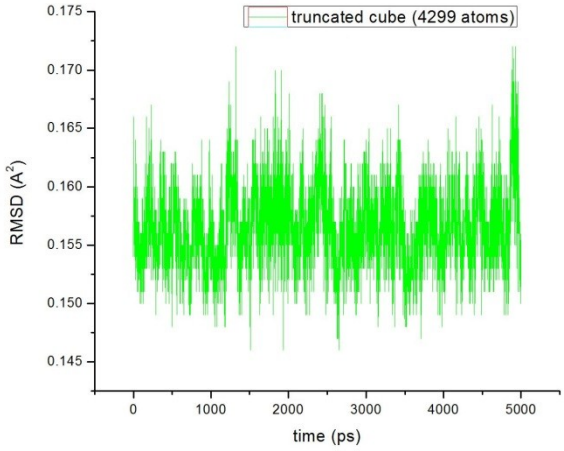
(a)


truncated cube (2197 atoms)
RMSD (A^2)
time (ps)

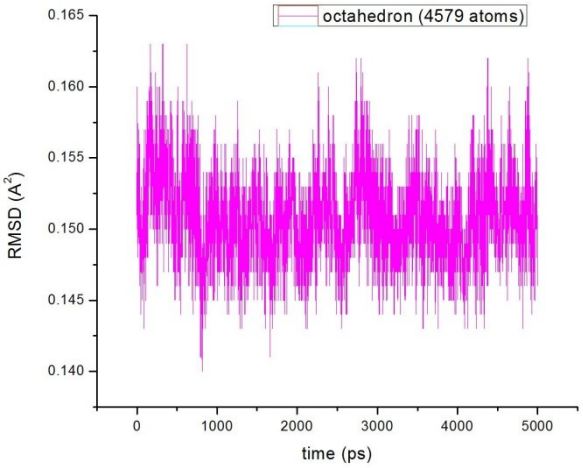
(b)


octahedron (2255 atoms)
RMSD (A^2)
time (ps)

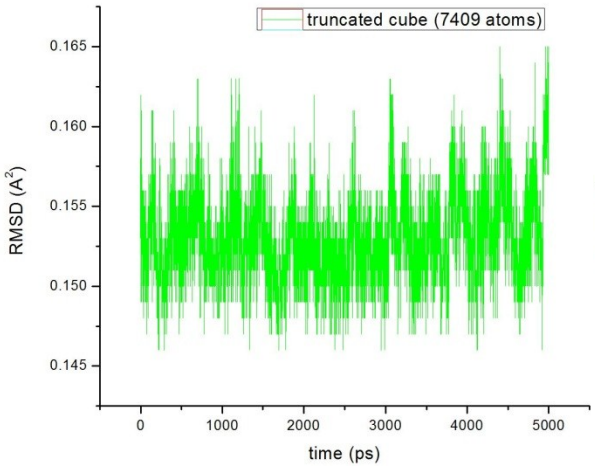
(c)


truncated cube (4299 atoms)
RMSD (A^2)
time (ps)

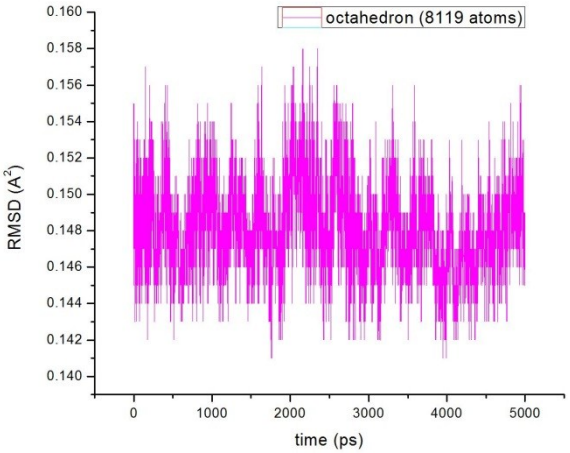
(d)


octahedron (4579 atoms)
RMSD (A^2)
time (ps)

(e)

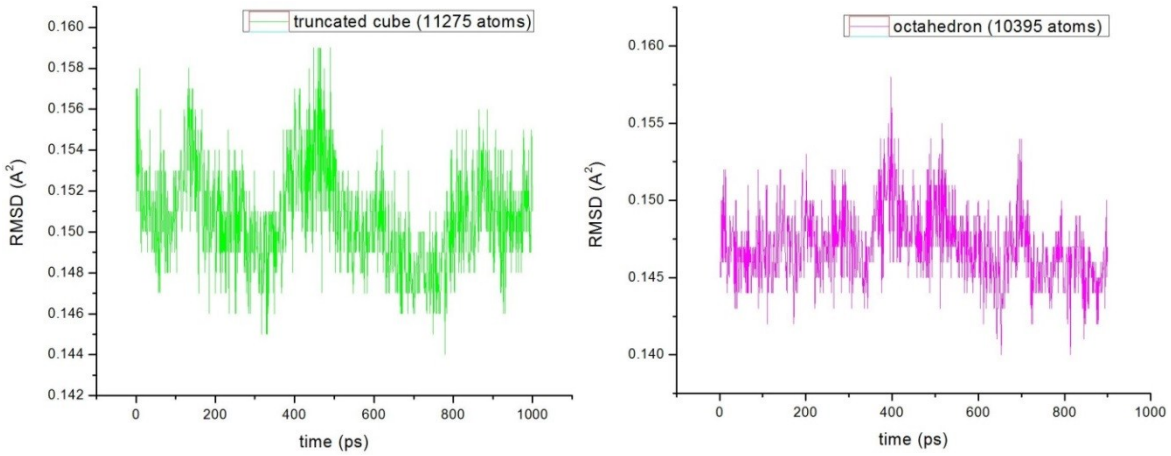

truncated cube (7409 atoms)
RMSD (A^2)
time (ps)

(f)


octahedron (8119 atoms)
RMSD (A^2)
time (ps)

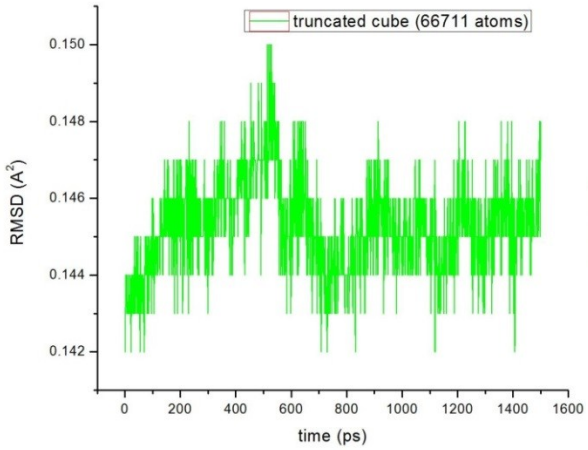
(g)

(h)

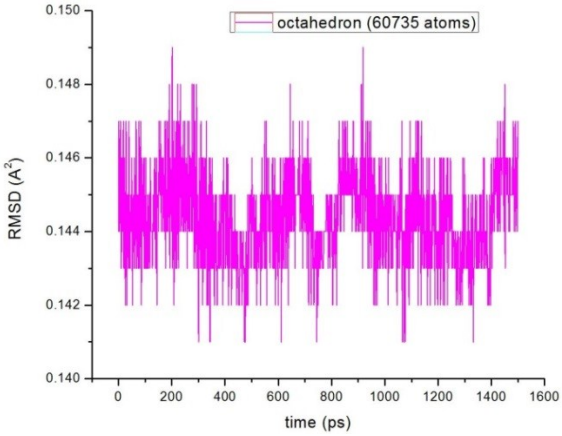


(i)

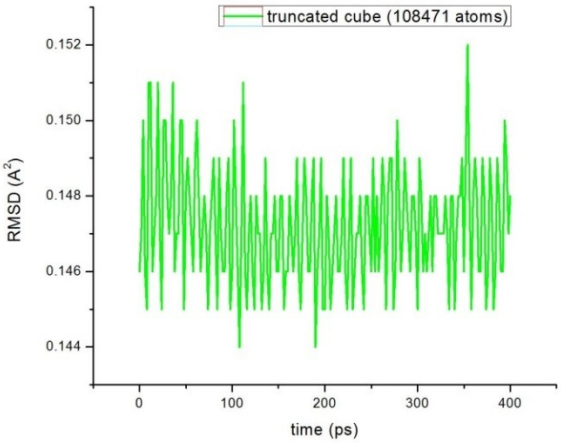
(j)



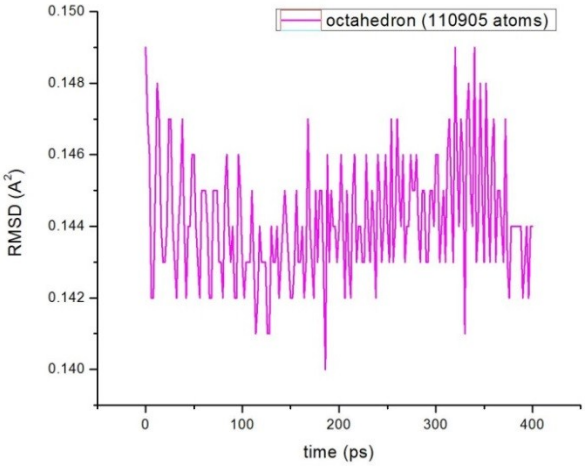
(k)



(l)



(m)



(n)

Fig S4. Stable RMSD for the NP's thermalized with MD. The figures in green represent the truncated nanocubes, while the figures in magenta correspond to the nano-octahedra. The number of atoms for each case is provided in the inset legend

3. Estimation of B_{iso} for experimental cube and octahedron

MD and DFT simulation were not made to provide exact values of MSD/B_{iso}: more than absolute values, the simulations are intended to explain the effect of nanocrystal size and shape and of capping agents, in particular on the static disorder of the nanocrystal surface. This is particularly useful in the comparison of our studied systems: Pd octahedra capped by CTAB, and truncated Pd nanocubes virtually 'clean', i.e., measured after careful removal of any capping agent.

As indicated by MD, one would expect the B_{iso} to be smaller for the octahedral than the cubes; this is partly due to the size, as octahedral are bigger than the cubes, and B_{iso} decreases with size, toward the bulk value (0.45 Å^2); but is also an apparently intrinsic feature of the shape, as the octahedral are enclosed by {111} facets, with higher coordination than the {100} facets of cubes. One way and/or the other octahedral should give a lower B_{iso}.

An estimate can be obtained by MD simulations, but the size of the crystals requires quite long calculations, and in any case we know that MD potentials cannot be exact or give values directly comparable with experiments. So we can make an assessment of B_{iso} values by considering the fraction of 'bulk', with B_{iso} = 0.45 Å^2, and add the fraction of surface, considered here as made of the three outermost layers, with the B_{iso} indicated by MD simulations run for smaller systems.

This corresponds to make (surface dynamic) + bulk, and gives 0.468 for octahedral, and 0.5003, that is B_{iso}(cubes) > B_{iso}(octahedra). B_{iso}(cubes) is in good agreement with the experimental value of 0.509(4) at T=300K. Concerning the octahedral, we put forward that the capping agent gives a rather strong contribution to the static disorder of the surface. This is indicated to be of the order of 1.25 Å^2 for CTAB on (111) Pd. This makes the dynamic contribution of the surface (made of the three outermost layers in our models) probably negligible. Indeed, if we add the DFT value for the static disorder effect of CTAB, correctly weighted for the fraction of surface atoms in the octahedral, we obtain, (surface static, due to adsorption) + bulk = 0.523 Å^2. More than the good match with the experimental value, 0.522(3), which is probably coincidental, here the relevant result is that MD and DFT simulations explain the higher B_{iso} of the octahedral with respect to the cubes, caused by the strong contribution of the capping agent to the surface static disorder.

Octahedron (experimental)

Approximate no. of atoms (from fitting XRD data) = 4,780,000

Approximate size (from fitting XRD data) = 53 nm

Surface static B_{iso} due to CTAB = 1.2508 Å^2

Estimated no. of surface atoms (3 outermost layers) = 435,000

Fraction of surface atoms, f_{surf} = 435000/4780000 = 0.091

Estimated B_{iso} = (surface static, due to adsorption) + bulk

= (0.114 + 0.409) Å^2

= 0.523 Å^2 (compared to 0.522 Å^2 from experiment)

Cube (experimental)

Approximate no. of atoms (from fitting XRD data) = 781,000

Approximate size (from fitting XRD data) = 23 nm

Estimated no. of surface atoms (3 outermost layers) = 142,700

Fraction of surface atoms, f_{surf} = 142700/781000 = 0.1827

Surface dynamic B_{iso} from MD (3 layers, calculated on smaller cube with 66711 atoms) = 0.725 Å^2

B_{iso} = surface dynamic + bulk

= (0.1325 + 0.3678) Å^2

= 0.5003 Å^2 (compared to 0.509 Å^2 from experiment)