Electronic Supplementary Material (ESI) for Nanoscale.
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Predicting the Role Seed Morphology in the Evolution of Anisotropic Nanocatalysts

Electronic Supplementary Information (ESI†)

Hector Barron*[1], George Opletal[1], Richard Tilley[2], and Amanda S. Barnard[1]

[1] *CSIRO, Molecular & Materials Modelling, Data61 CSIRO, Door 34 Goods Shed, Village St, Docklands, Victoria, 3008, Australia*

[2] *University of New South Wales, Sydney, 2052, NSW, Australia*

1 Simulation Details

Simulations were performed with LAMMPS [1] by Classical Molecular Dynamics (MD) in use of an Embebedd-Atom-Method (EAM) force field developed by Adams and Foiles [2] In order to study the nucleation process, initial seeds were constructed from original FCC crystalline Pt nanoparticles obtaining cubic, cuboctahedral and icosahedral shapes. Each of these initial seeds consists of 1098, 1414 and 1415 atoms respectively. An energy minimisation process is performed for each initial seed before the simulation started. The simulation was carried out within the microcanonical ensemble (NVE) using a Langevin thermostat and no periodic boundary conditions was applied. The Verlet's leapfrog algorithm for integrating Newton's equations of motion was used in all the simulations. The nucleation simulated process consists in the addition of single Pt atoms at atomic deposition rate of 1 atom each 100 simulation steps ($\tau = 5 \times 10^{-4}$ atoms per ns) during 10 ns with a time step of 5 fs. The temperature range in this study is from 0 to 27, 0 to 327 and 0 to 727 Celsius for each initial seed.

*email: hector.barronescobar@data61.csiro.au

2 Cohesive Energy

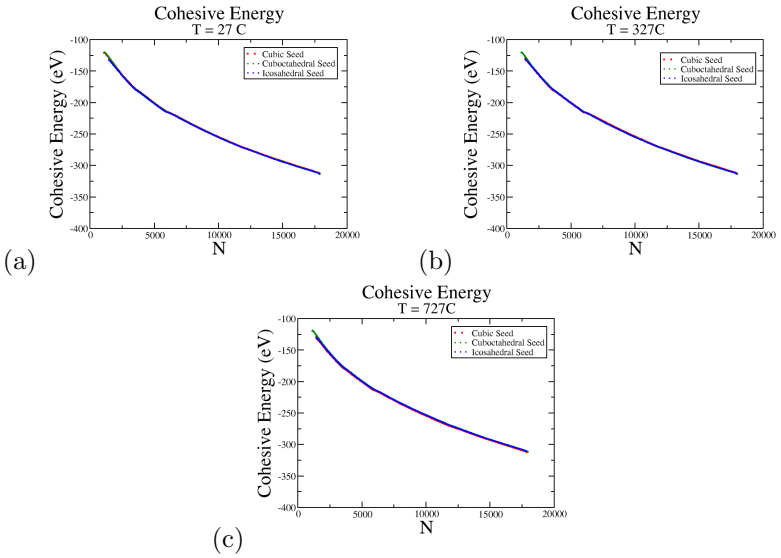

Figure S1: Cohesive energy as a function of the size N: (a) at 27°C, (b) 327°C and (c) 727°C. Curves in red correspond to the cohesive energies for Cubic seeds, green curves correspond to Cuboctahedral seeds and blue curves to Icosahedral seeds. We calculate the binding energy (as in reference [3]) of the three initial seeds during the nucleation process to compare the stability of clusters at different size ranges. As can be seen, the relative stability of this structural growth pattern is similar between the three initial seeds for all temperatures. This similar stability is explained by the large surface defects formed during the nucleation, that in all cases, leads the formation of non-crystalline structures.

3 Cross Section Images of the Final Simulated Pt Nanoparticles

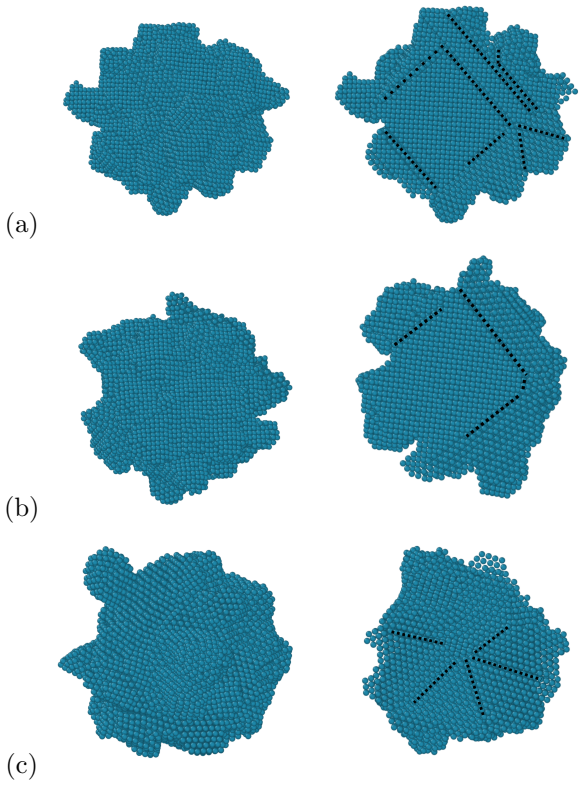

Figure S2: Atomistic models and their corresponding cross section image (right side) of the final Pt nanoparticles obtained at 27°C. (a) Snapshot of the final structure with initial cubic seed, (b) a snapshot of the final structure obtained with initial cuboctahedral seed, and (c) a snapshot of the final structure obtained with icosahedral initial seed. In all cases the inner part of the particle exhibit atoms arranged in FCC fashion. In addition, we can observe the formation of dislocations, vacancies, terraces and steps (dashed lines) in the inner core and in the case of the icosdahedral initial seed re-entrant edges and twins are also noticeable.

4 Snapshots of the Nucleation Process with Different Initial Seeds

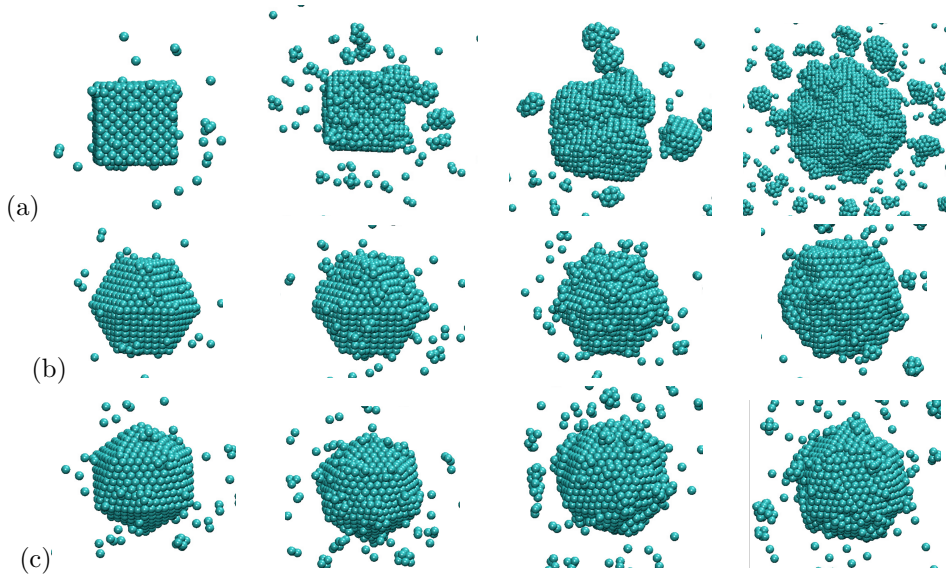

Figure S3: Atomistic models of the nucleation process of Pt nanoparticles at $T = 27°C$. The sequence (a) to (c) shows the moment in which the initial symmetry of the seed is vanish by the adsorption/desorption of atoms and small clusters on the particle surface; the formation of small clusters as a consequence of sintering and coalescence between Pt atoms are also observable. Snapshots of the nucleation process with a) cubic initial seed at 0.02, 0.03, 0.99 and 4.39 ns respectively, b) cuboctahedral initial seed at 0.02, 0.07, 0.12 and 0.74 ns respectively, and c) with icosahedral initial seed at 0.05, 0.12, 0.25 and 0.55 ns respectively.

References

[1] http://lammps.sandia.gov.

[2] Foiles, S. M.; Baskes, M. I.; Daw, M. S., Embedded Atom Method Functions for the FCC Metals Cu, Ag, Au, Ni, Pd, Pt, and their Alloys. *J. Phys. Rev. B*, **1988**, *33*, 7983-7991.

[3] Baletto, F.; Ferrando, R., Structural properties of nanoclusters: Energetic, thermodynamic, and kinetic effects. *Rev. Mod. Phys.*, **2005**, *77*, 371-417.