

# Supplementary Materials for

## **3D** structure of individual nanocrystals in solution by electron microscopy

Jungwon Park, Hans Elmlund, Peter Ercius, Jong Min Yuk, David T. Limmer, Qian Chen, Kwanpyo Kim, Sang Hoon Han, David A. Weitz, A. Zettl, A. Paul Alivisatos\*

\*Corresponding author. E-mail: alivis@berkeley.edu

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This PDF file includes: Molecular Dynamics Simulation Materials and Methods Figs. S1 to S9 Captions for movies S1 to S4

Other supplementary material for this manuscript includes:

Movies S1 to S4

#### **Captions for Movies S1 to S4**

Movie S1. 3D EM density map of particle 1.

Movie S2. 3D EM density map of particle 2.

**Movie S3.** TEM movie of Pt nanoparticles in GLC. The movie is composed of 200 subsequent non-averaged frames with the full field of view binned by 2.

**Movie S4.** TEM movie of Pt nanoparticles in a small section of the full field of view at full resolution. The section of interest is selected from the lower right quadrant of Movie S3.

#### **Molecular Dynamics simulation**

The width of a grain boundary can be computed by determining local volumes surrounding atoms in a structure using a Voronoi tessellation (29). For a (110)-(100) grain boundary, similar to that between the upper and core sections of particle 1, this width is around 5 Å (Figure S7 (A) and (B)). Any additional grain boundaries in the nanoparticle that are not overlapping with this interface, as is the case for the three domain structure observed, have additive contributions to the free energy of the nanoparticle. The surface free energy for the ligand-exposed interfaces was computed to be 2.8 J/m<sup>2</sup> as averaged over the (100) and (111) surfaces, weighted appropriately for the cuboctahedral shape. The disparity of scales between the grain boundary free energies and the much larger exposed surface free energies confirms that there is a large thermodynamic driving force for coalescence, even when such events result in grain boundary formation. For example, aggregating three N = 400 particles into a single N =1200 crystal is favored by -11.3 kJ/mol for a single crystalline structure and -8.2 kJ/mol for a three-domain-structure, such as those observed here. In both cases, the free energy gain per particle is much larger than typical thermal energies, likely rendering the initial aggregation irreversible. Small relative rotational distortions of the crystal grains are

found to be energetically viable for (110)-(100) interfaces, which may explain their prevalence in our structures. As detailed in the supporting information, similar thermodynamic driving forces exist for aggregation along other low-index crystallographic axes and for other size particles (Figure S7 (C) and S8), consistent with previous observations (Figure S8) (3, 5). For larger nanoparticles, slow surface diffusion and the tight packing of adsorbed ligands are likely to kinetically mediate these large thermodynamic driving forces. However, for smaller nanoparticles that are likely to be involved in aggregation, such steric effects have been shown previously to be less important and do not saturate all potential surface binding sites (4, 30). In all cases, the resultant planar grain boundaries have slow relaxation at room temperature and once formed they are kinetically arrested over experimental timescales.

#### **Materials and Methods**

#### Verification of the 3D reconstruction method with simulated Pt crystal structure

To verify that our 3D reconstruction methodology is capable of producing near-atomic resolution reconstructions, we generated 1000 randomly oriented projection images of a simulated symmetrical Pt nanocrystal with dodecahedral symmetry. The images were generated with multi-slice simulation (*31*), using the input parameters  $C_3$  of -10 µm,  $C_5$  set to 1.0 mm, a defocus of 37 Å, an objective limit of 20 mrad, a convergence angle of 0.5 mrad, and a defocus spread of 50 Å, and a slice value of 1 Å. The pixel resolution of the simulated images was 0.58 Å to match the pixel resolution of the experimental images. Gaussian noise was added to the images to give a signal-to-noise ratio (SNR) of 0.2, roughly corresponding to the SNR of the individual experimental frames. The simulated images were processed by PRIME exactly as for the experimental images as described above. The final reconstruction had a resolution of 2.5 Å and showed the expected dodecahedral symmetry (Fig. S2). The point group symmetry was not used as *prior* information—the probabilistic (or weighted) orientation assignment in PRIME automatically identifies the point-group symmetry without it being imposed as a

constraint in the orientation search. The same behavior was observed in the past when processing cryo-EM images of D2 and D7 symmetrical molecules.

#### Sample preparation of Pt nanocrystal solution

Pt particles dispersed in solution for GLC TEM series acquisition can be prepared by two methods. Pt particles can be synthesized and dispersed in solvent prior to the encapsulation in GLC.

Pt nanoparticles with sub-2 nm size are synthesized by following a previously reported method with modifications (32). 10 mL of tetra-n-octylammonium bromide solution (0.05 M, 0.273 g in 10 mL) in toluene is added dropwise into a round-bottomed flask containing an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (0.03 M, 0.00648 g in 3.75 mL H<sub>2</sub>O). Then, the mixture is stirred for 10 min with a magnetic stirring bar. An aqueous solution of sodium borohydride (0.4 M, 0.0529 g in 3.5 mL H<sub>2</sub>O) is quickly injected into the reaction mixture. The pale-yellow organic phase immediately turns into brown which indicates the formation of Pt nanoparticles. After 30 sec from the injection of sodium borohydride, 51  $\mu$ L (2.50 × 10<sup>-4</sup> mol) of dodecanethiol is added. The mixture is subsequently stirred for 3 h, followed by separation of the organic phase using a separation funnel. 40 mL of ethanol is added to the organic solution containing the nanoparticles, and the mixture is maintained in a freezer for 1 h to allow precipitation of the particles. The particles are then separated by centrifugation (6000 rpm for 20 min), washed several times with a mixture of ethanol and acetone. As-synthesized Pt particles are soluble in organic solvents for the preparation of a graphene liquid cell. The particle solution is diluted to half of the concentration by using a mixture of o-dichlorobenzene and oleylamine with a volume ratio 20 to 1. The final particle solution in a mixture of odichlorobenzene and oleylamine maintains its colloidal stability for liquid phase TEM for longer than 6 months.

Graphene liquid cell preparation

Graphene is synthesized by chemical vapour deposition (CVD) on 25  $\mu$ m thick copper foil (99.8 %, Alfa Aesar, Ward Hill, MA). The copper foil is inserted into a quartz tube and heated to 1,000 °C under a H<sub>2</sub> flow of 10 cm<sup>3</sup>/min at 150 mTorr. After annealing for 30 min, a gas mixture of 25 cm<sup>3</sup>/min CH<sub>4</sub> and 10 cm<sup>3</sup>/min H<sub>2</sub> at 520 mTorr is introduced for 20 min to synthesize graphene. Fast cooling to room temperature with a CH<sub>4</sub> flow of 20 cm<sup>3</sup>/min under a pressure of 330 mTorr follows.

The synthesized graphene on Cu foil is transferred to Quantifoil holey C TEM grids using a direct transfer method (33). In brief, a graphene-covered Cu foil is placed onto a glass slide and gently flattened by pressing with another glass slide. Graphene on the exposed side is removed by mild O plasma etching. The Quantifoil TEM grid is placed onto a graphene side of Cu foil with the Quantifoil C film side facing the graphene. Then 10.0 µl of isopropyl alcohol is dropped onto the sample to wet the interface, and the sample is dried at 80 °C on a hot plate for 20 min to promote adhesion between the Quantifoil C film and the graphene. The grid is floated on an aqueous solution of 113 mM ammonium persulfate,  $(NH_4)_2SO_4$ , to etch the underlying Cu foil and rinsed several times by floating the graphene transferred grid on deionized water. Two graphene coated holey C film TEM grids are prepared using this method. For encapsulation of the liquid sample, 0.5 µl of either Pt growth solution or synthesized Pt particle solution is placed onto one graphene coated TEM grid that is held by self-closing tweezers. A small portion of the edge of the other graphene coated TEM grid is cut by a razor blade to promote a close contact between the two graphene sheets when it is placed on the TEM grid held by the tweezers tip. The partially cut graphene TEM grid is gently placed onto the graphene TEM grid with the sample solution and left in ambient conditions for several hours to promote solvent drying mediated bonding between two graphene surfaces. As-prepared graphene liquid cells are plunged into isopropanol solution to clean off the excess solution and then dried in ambient conditions.

Acquisition of movies of Pt nanoparticles

The images were acquired using TEAM I, an FEI Titan 80/300 transmission electron microscope (TEM) with a post-specimen geometric- and chromatic-aberration corrector at the National Center for Electron Microscopy within The Molecular Foundry. The aberration-corrector was aligned for approximately -10  $\mu$ m third-order spherical aberration (C<sub>3</sub> or C<sub>3,0</sub>) to produce white atom contrast at a small under focus value of 30 – 50 Å (*34*). The detector used is a prototype of the Gatan K2-IS direct electron detector with 1024 x 1024 pixels with superior contrast transfer and ~50 frames-per-second (fps) acquisition capability (*18*). Liquid pockets that were used in imaging are in the diameter range of sub-50 nm. It was necessary to sum 5 images to provide sufficient SNR for the reconstruction algorithm.

#### Molecular dynamics simulation

**Calculation Details** To represent a Pt nanocrystal, we start with an ideal cuboctahedral shape. This shape is predicted from simple thermodynamic arguments that minimize the relative surface free energies given different solvent exposed crystal facets and a size constraint. These equilibrium constructions yield stable cuboctahedral structures for a range of nanocrystal sizes (35). Interactions between Pt atoms are modeled with the embedded atom model (EAM) (36), which is based on a second moment expansion of a tight-binding expression for the energy of a delocalized electronic system. Its functional form can be written as a sum of pair functions and a many body function dependent on the local density

$$U(\mathbf{r}^{3N}) = \sum_{i < j} \phi(r_{ij}) + \sum_{i} f\left(\sum_{j} \rho(r_{ij})\right)$$
(1)

where  $\phi(r)$  is a pair function,  $\rho(r)$  is a local density function and  $f(\rho)$  is the embedding function. The forms of these functions are quintic splines with smooth second derivatives and asymptote to zero to insure non-impulsive forces and typically fit to *ab initio* data. EAM potentials have been use previously with much success in modeling surface reconstruction and deformation in metallic systems. The potential we adopt for Pt was developed by Sheng et al., parameterized with first principles data and optimized with a host of experimental reference data including lattice constant and vacancy formation energies (28). Of particular relevance to this study is the accurate recovery of the bulk Young's and shear moduli at low temperature and stacking fault energies.

To compute the grain boundary free energy, we use the Frenkel-Ladd model and construct a thermodynamic integration path that references an ideal harmonic, or Einstein, crystal (27). The schematic path is illustrated in Fig. S7. Specifically, we compute the reversible work to transform a defect-free nanocrystal into one with a symmetric planar twist grain boundary along one of the lower index crystal planes, (100), (111) or (110), characterized by a misalignment angle. We do this in three steps. First, we compute the free energy of the defect-free nanocrystal interacting with the EAM potential relative to a purely harmonic system with the same geometry. We do this by thermodynamic integration,

$$\mathcal{H} = U(\mathbf{r}_{h}^{3N}) + (1 - \lambda) \left( \Delta U(\mathbf{r}^{3N}, \mathbf{r}_{p}^{3N}) \right) + \lambda \sum_{i} \alpha (r_{i} - r_{p,i})^{2}$$

$$(2)$$

where  $r_p^{3N} = \{r_{p,1} \dots r_{p,N}\}$  are the positions of all atoms in the ideal nanocrystal,  $\Delta U(r^{3N}, r_p^{3N}) = U(r^{3N}) - U(r_p^{3N})$  and  $\lambda$  varies between 0, where the system interacts with the EAM potential, and 1 where the system is composed on non-interacting harmonic oscillators. The free energy, different for adiabatically changing from the system defined by  $\lambda = 0$  to  $\lambda = 1$ , can be calculated from

$$\Delta F_{1,2} = \int_0^1 d\lambda \, \langle \frac{d\mathcal{H}}{d\lambda} \rangle_\lambda$$
$$= \int_0^1 d\lambda \, \langle \sum_i \alpha (r_i - r_{p,i})^2 - \Delta U \big( \mathbf{r}^{3N}, \mathbf{r}_p^{3N} \big) \rangle_\lambda. \tag{3}$$

The benefit of doing this is that the free energy for an ideal harmonic system in 3 dimensions is known exactly and is given by

$$F_2 = U(\mathbf{r}_p^{3N}) - \frac{3k_{\rm B}T}{2}N\ln(k_{\rm B}T\pi/\alpha),\tag{4}$$

where  $k_{\rm B}$  is Boltzmann's constant and *T* is the temperature, here 300 K. Computing the free energy difference between the defect-free nanocrystal and one with a grain boundary for a purely harmonic system with the same number of degrees of freedom and the same spring constants is then,

$$\Delta F_{2,3} = \Delta U \left( \mathbf{r}_d^{3N}, \mathbf{r}_p^{3N} \right), \tag{5}$$

where  $r_d^{3N}$  are the positions of the atoms for a nanoparticle with a grain boundary. Finally the free energy for transforming the nanocrystal with a grain boundary from a harmonic reference to a fully interacting system is the same as Eq. 3,

$$\Delta F_{3,4} = -\int_0^1 d\lambda \left\langle \sum_i \alpha \left( r_i - r_i^h \right)^2 - \Delta U(\mathbf{r}_d^{3N}, \mathbf{r}_h^{3N}) \right\rangle_\lambda ,$$
(6)

but with  $r_p^{3N}$  replaced by  $r_h^{3N}$ . The total grain boundary free energy is then given by the sum

$$\Delta F_{\rm GB} = \Delta F_{3,4} + \Delta F_{2,3} + \Delta F_{1,2} .$$
(7)

In order to evaluate the integrals in Eq. 3 and 5, we must discretize the path. To do so we follow de Koning and Antonelli by choosing points along the curve defined by

$$\lambda(\tau_i) = \tau_i^5 (70\tau_i^4 - 315\tau_i^3 + 540\tau_i^2 - 420\tau_i + 126),$$
(8)

where  $\tau_i = i/p$  is the *i*th path of *p* total sampling points (37). This places additional sampling on the lower and higher ends of  $\lambda$  where effects due to unconstrained center of mass motion can lead to rapid variations in the integral.

Symmetric grain free energies We have computed  $\Delta F_{GB}$  as a function of misalignment angle  $\Theta$ , which we denote  $\Delta F(\Theta)$ , for the low index crystal planes (100), (111) and (110).

The results of these calculations for a N = 1135 atom nanoparticle is shown in Fig. S9, where we have normalized each curve by the area of the grain boundary  $\Upsilon(\Theta) =$  $\Delta F(\Theta)/A$ , in such a way that the asymptotic value for large nanoparticles is consistent with a bulk grain boundary free energy computed with periodic boundary conditions. Each crystal plane has a different symmetry. The (100) surface is four-fold symmetric and as a result  $\Upsilon(\Theta)$  has a period of 90°. Approaching 45°,  $\Upsilon(\Theta)$  is monotonically increasing and fairly featurelessbefore decaying back to 0 at 90°. The (111) surface is three-fold symmetric and as a result  $\Upsilon(\Theta)$  has a period of 120°. The (111) surface is close-packed and as a result the free energy as a function of  $\Theta$  is fairly featureless, reaching a flat profile at 20° before decaying back to 0 at 90°. The maximal value of the (111) surface relative to the (100) surface is greater by a factor of 2, as has been observed previously. At 60°, there is a sharp dip in the free energy, which reflects the formation of a coherently twinned plane common to all FCC lattices, whose energy is much lower than a grain boundary's. The (110) surface is two-fold symmetric and as a result  $\Upsilon(\Theta)$  has a period of 180°. This surface exhibits a much richer structure than either of the more closed-packed surfaces as a function of misalignment. Specifically, there are symmetric meta-stable minima at 70° and 110° separated by large free energy barriers. These minima are due to the formation of incoherently twinned planes. Further, the corrugation of the (110) surface results in an overall higher surface free energy relative to the (100) or (111) surfaces. The cusps found in each of these functions are similar as those found in bulk materials (38).

Asymmetric grain, (110)-(100), free energies We have also computed  $\Delta F_{GB}$  for an asymmetric, (110)-(100), grain boundary like that found in our experiment. The results of this are shown in Fig. 6. As an asymmetric grain boundary, even with 14<sup>o</sup> misalignment between relative [111] surface directions, there is a nonzero free energy of 0.3 J/m<sup>2</sup>. This free energy increases to 0.55 J/m<sup>2</sup> at relative orientations of 59° before decreasing consistent with the 4-fold symmetry of the (100) surface. These values contain contributions both from in-plane disordered packing as well as surface stresses from the

line defect circumscribed at the boundary. Thus, the packing at the interface determines the overall excess free energy.

Width of the grain boundary Using a Voronoi tessellation, the local volume around each atom can be computed. The distribution of volumes cleanly distinguishes between interior and surface atoms. Fig. S8 (A) and (B) show the excess volume is localized near (110)-(100) grain boundary at z = 0. The width of the interface is ~ 5 Å as determined by the full-width at half max of a Gaussian fit to the profiles. The localization of excess volume near a grain boundary is a signature of disrupted packing. Moreover, we have found that an additional grain boundary in the nanoparticle, as determined by the excess volume, has additive contributions to the free energy of the nanoparticle.

**Ligand exposed surface free energies** In order to determine the excess surface free energy of a single grain nanocrystal, we analyze the finite size scaling of the free energy of cuboctahedral nanoparticles. This is done with the thermodynamic path in Fig. S7, where only steps 1 and 2 are necessary, with particle sizes between 100 and 30000 atoms. In order to extract the chemical potential and surface free energy of the Pt atoms, we fit the free energy to the form,

$$F(N) = \mu N + f_s N^{2/3},$$
(9)

where  $\mu$  is the chemical potential and  $f_s$  is the non-extension contribution to the free energy, which is expected to be of the form of an exposed surface tension times a specific area reflective of the cuboctahedral geometry. The data and fit are shown in Fig. S8 (C), where f(N) = F(N)/N. This fit yields a value of  $f_s = 308$  kJ/mol. Using the values of the maximal coverage and binding energy of oleylamines from the reference (30), we can approximately correct the excess surface energy for ligand coverage, assuming that entropic effects from ligand packing are negligible. This yields  $f_{s,l} = 270$  kJ/mol.

Thermodynamic driving force for aggregation Using the data computed above, the

thermodynamic driving force for aggregation can be determined. This is done by considering an expression for the free energy difference between a nanoparticle of size N and an aggregate made up of a multiple of nanoparticles  $N_b$  with b independent grain boundaries. The following generic form follows, assuming a constant geometry,

$$\Delta F_{\text{agg}} = f_{s,l} \left[ N_b N^{2/3} - (N_b N)^{2/3} \right] - b f_g (N_b N)^{2/3},$$
(10)

where  $f_g$  is the grain boundary free energy for a specific crystal direction times a specific area for the grain boundary. In Eq. 10 volume terms proportional to a chemical potential drop out, and we have neglected logarithmic corrections associated with the reduction of entropy due to aggregation. From the free energies above, the maximal grain boundary free energies for symmetric grains are  $f_g^{110} = 38$  kJ/mol,  $f_g^{100} = 22$  kJ/mol,  $f_g^{111} = 12$ kJ/mol, and for the asymmetric (110)-(100) grain is  $f_g^{110-100} = 25$  kJ/mol. With Eq. 10 and the parameters above, the thermodynamic driving force for aggregation can be computed. Generalization for aggregates of non-similar sizes is straightforward. Note that the scaling analysis done here does not require a definite determination of the volume or surface area of the nanocrystal, as typically such measures are ill-defined.

### **Supporting Figures**



**Fig. S1.** Validation of the 3D reconstruction methodology using simulated data of a dodecahedral Pt nanoparticle. (**A**) Reconstruction from images without noise (top panel) and representative images (bottom panel). (**B**) Reconstruction from images with a SNR of 0.1 (top panel) and representative images (bottom panel).



**Fig. S2.** Power spectra and orientation coverage for particle 1 and 2. Orientation coverage is extracted by the projection orientation vector onto the horizontal plane. Particle 2 series shows better rotational coverage than particle 1 series, which suffers from a missing wedge of information.



**Fig. S3.** Validation of the 3D reconstruction for particle 1 and particle 2. (**A**), (**B**) Comparison of frame averages (left column) with re-projections of the map (right column) for particle 1 and 2, respectively. (**C**), (**D**) The diagrams show the average Fourier Ring Correlation (FRC) between the images and the re-projections for particle 1 and 2, respectively. The FRC is larger than 0.143 to 1 Å resolution and shows a distinct peak spanning the 1-2 Å region. This peak is due to the correlation between atomic densities in the re-projections and atomic densities in the images.



**Fig. S4.** Slabs through the density maps of (A) particle 1 and (B) the particle 2 along the vertical cross-sections with different depths: behind the mid-plane (left), at the mid-plane (middle), and the front plane (right). Whereas straight lattice planes are clearly seen in multiple domains of particle 1, particle 2 shows more disordered internal structures. It is difficult to specify the exact atomic arrangement, since the current resolution is slightly anisotropic. However, the presence of additional domains and edge dislocations are likely causes of such disordered lattice patterns.



**Fig. S5.** Slab through images of particle 2 along the horizontal cross-sections with different depths: above the equatorial plane (top), at the equatorial plane (middle), and below the equatorial plane (bottom).



Fig. S6. Schematic thermodynamic integration path for computing twist grain boundary free energies characterized by a crystal face and misalignment angle,  $\Theta$ .



**Fig. S7.** (**A**) The average Voronoi cell volume as a function of displacement from the center of the nanocrystal, where the grain boundary originates. Three different color curves represent these distributions for three different initial misalignment angles. (**B**) Cross-sectional view of the relaxed nanocrystal with an initial misalignment angle  $14^{\circ}$ . Blue-to-red color gradient scales decreasing Voronoi cell volume from near to away the grain boundary as observed in the plot for  $14^{\circ}$  in (A). Surface atoms show a high cell volume due to unsaturated coordination. (**C**) The scaling behavior of the specific free energy per particle computed from thermodynamic integration of a cuboctahedral nanoparticle. The solid red line is a fit to the form in Eq. 9.



Fig. S8. Twist grain boundary free energies as a function of misalignment angle for the (100), (111) and (110) crystal planes of a N = 1135 atom nanocrystal. The grain boundaries are located in the center of the nanocrystal. Shaded regions indicate error bars of 1 and 2 standard deviations.