Supplementary Information for Sudden collective atomic rearrangements trigger the growth of defect-free silver icosahedra

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1 Comparison between experimental and simulated GIWAXS spectra

The 1D experimental scattering profile was compared with simulated patterns obtained from calculated model clusters on the basis of the Debye equation [1,2] and considering the set-up geometry using a dedicated home-made software [3]. Preliminary to the in situ deposition of clusters on each sample, the reference pattern from the substrate without particles was measured in the same conditions. The model clusters of icosahedra (Ih), decahedra (Dh) and truncated octahedra (TOh) were obtained from Monte Carlo (MC) and molecular dynamics (MD) simulations, at various temperature using a semi-empirical tight-binding potential. A weighted sum of the intensities from several sizes or structures was used to fit the WAXS patterns considering the size distribution coming from GISAXS results already performed simultaneously. Only the type of structure (not the size distribution) is adjusted to fit with the experimental spectra. Fig. S1a shows an experimental GIWAXS

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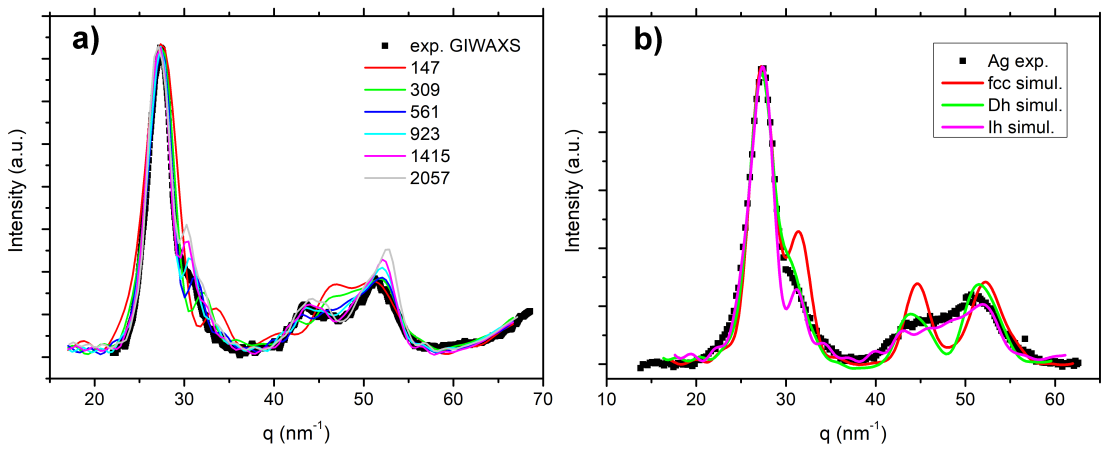

Figure S 1: Two GIWAXS experimental spectra of Ag nanoparticle assembly coming from 2 different measurements in the similar range of 2-2.5 nm in size during the UHV growth (dots), with the superimposition of simulations of several simulated spectra: a) from an Ih model of 561 atoms, a Dh model of 585 atoms and a TOh model of 405 atoms (lines). b) from a set of Ih models of sizes from 147 to 2075 atoms.

spectrum example and a set of simulated spectra corresponding to several sizes of Ih Ag clusters (from 147 to 2057 Ag atoms). In this example (see the final fit in Fig. 1b), the models which better fit the experimental data are those from Ag_{309} to Ag_{923}, which indicates that the majority of clusters in the experimental sample is in this size range. This is in agreement with the measured distribution obtained by GISAXS spectra. In this fit, the part of non-Ih structures is negligible (less than 10%).

In Fig. S1b an experimental GIWAXS spectrum of clusters grown at room temperature is compared with simulated spectra of an icosahedron, of a decahedron and of a truncated octahedron. The spectra from the Dh and TOh are very far from the experimental data. In this figure we consider only size 561 for the Ih. However, this single-size spectrum is already in very good agreement with the experiment, and in much better agreement than simulated Dh and TOh spectra.

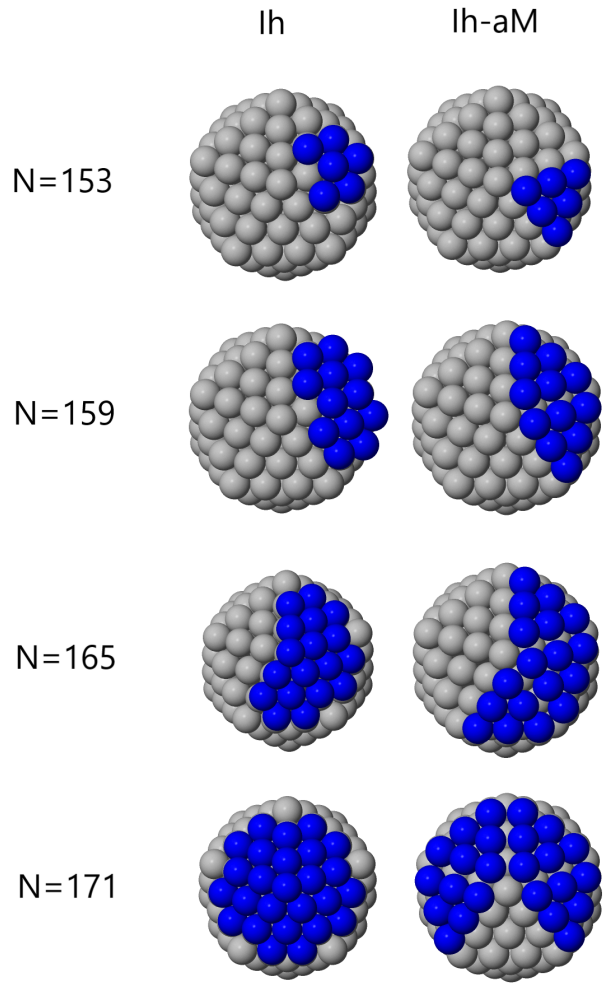

Figure S 2: Icosahedra of 147 atoms (grey spheres) covered by Mackay islands (left column) and anti-Mackay islands (right column). The atoms of the islands are coloured in blue. The energy differences between these structures is reported in Table 1 of the main text.

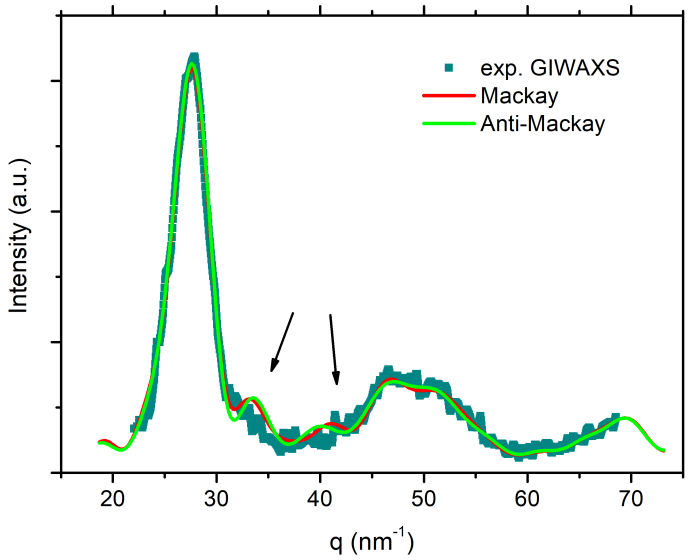

Figure S 3: Simulated GIWAXS spectra (lines) of icosahedra models of 165 atoms with Mackay and with Anti-Mackay shell. The main but weak differences are indicated by two arrows in the spectra. A GIWAXS experimental spectrum of Ag nanoparticle assembly measured during the UHV growth (dots) is showed for comparison. The range of 1.7 nm in average size is near the 165 atoms size of cluster models with Mackay and with Anti-Mackay shell used for the GIWAXS simulations.

2 Mackay and anti-Mackay islands for DFT calculations

In Fig. S2 we report the configurations of the Mackay and anti-Mackay islands used for the calculations of Table 1 of the main text.

3 Simulated GIWAX spectra of icosahedra with Mackay and anti-Mackay incomplete shell

In Fig. S3 we compare the simulated GIWAXS spectra of two of the model icosahedral nanoparticles shown in Fig. S2. The two nanoparticles have the same size (165 atoms) and they differ for the stacking of the incomplete outer shell (Mackay or anti-Mackay). Differences in the spectra from single size models are weak, and are expected to become even weaker if the size distribution

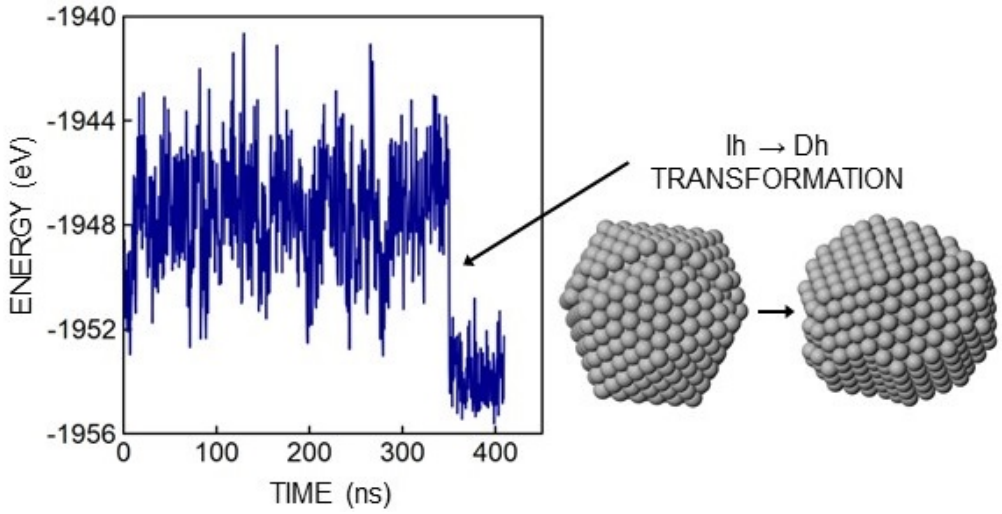

Figure S 4: Left panel: energy as a function of time in a simulation starting from an icosahedral structure and transforming into a decahedron. The simulation temperature is 760 K.

of the nanoparticle sample is taken into account. Therefore, it is is unrealistic to hope to detect the transformation from the anti-Mackay to the Mackay arrangement during the Ag nanoparticle growth by X-ray experimental measurement, as predicted by molecular dynamics simulations.

4 Ih→Dh transformation upon annealing.

In Figs. S4 and S5 we report results of annealing simulations of icosahedral structures of 700 and 191 atoms. These structures are at the upper and lower size limit of those grown in the experiments. In Fig. S4 the as-grown icosahedron of 700 atoms has been evolved at a constant temperature of 760 K. The transformation into a decahedral structure occurs after $\sim$340 ns by a sudden collective rearrangement. The tranformation of Ih structures upon annealing has been studied by MD simulations also for the case of an as-grown Ih cluster of 191 atoms with annealing temperatures is the range 500-600 K. For each temperature, 20 independent simulations have been made, stopping them at the transformation of the Ih structure, which, in almost all cases, has been towards a Dh structure of the type shown in Fig. 5. The times of the transformation have been averaged to

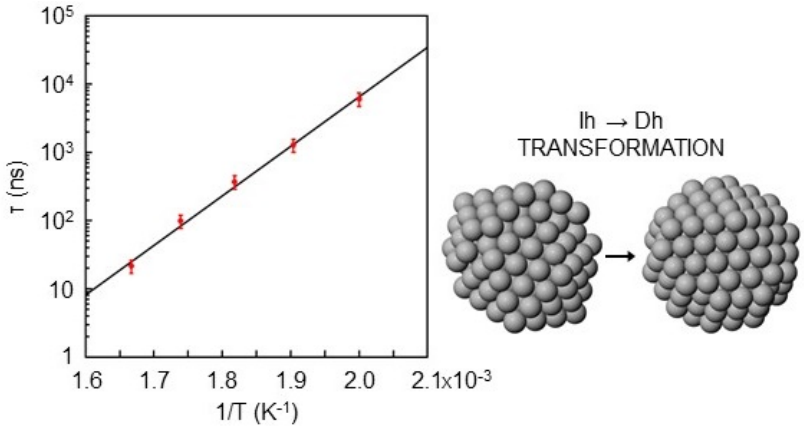

Figure S 5: Arrhenius plot of the lifetime of an as-grown Ih structure of 191 atoms which transforms into a Dh structure.

calculate the lifetime τ of the Ih structure at the different temperatures. The values of τ very well accommodate on an Arrhenius behaviour as shown in Fig. 5, whose extrapolation to RT gives a lifetime of about 10 h. This time scale is compatible with the ageing times of the experiments.

5 Growth on top of an anti-Mackay structure

In Fig. S6 we report snapshot of a simulation which starts from a icosahedral clusters (top row of Fig. S6), made of a Mackay icosahedron of 147 atoms covered by a first shell made of 20 anti-Mackay triangular islands (blue atoms), for a total of 267 atoms. In each island, three atoms are kept fixed in their initial positions so that the islands cannot shift from the anti-Mackay stacking. Atoms are deposited on this structures at a temperature of 500 K and a rate of 1 atom every 10 ns to reach the final size of 561 atoms. The final structure is quite irregular and rough (see the snapshots in the bottom row of Fig. S6), with a third shell (red atoms) already growing on top of an incomplete and quite disorder second shell (yellow atoms). The comparison of these results with those of Fig. 3 of the main text demonstrates that in the absence of the aM$\rightarrow$M transformation the clusters would grow much rougher and disordered.

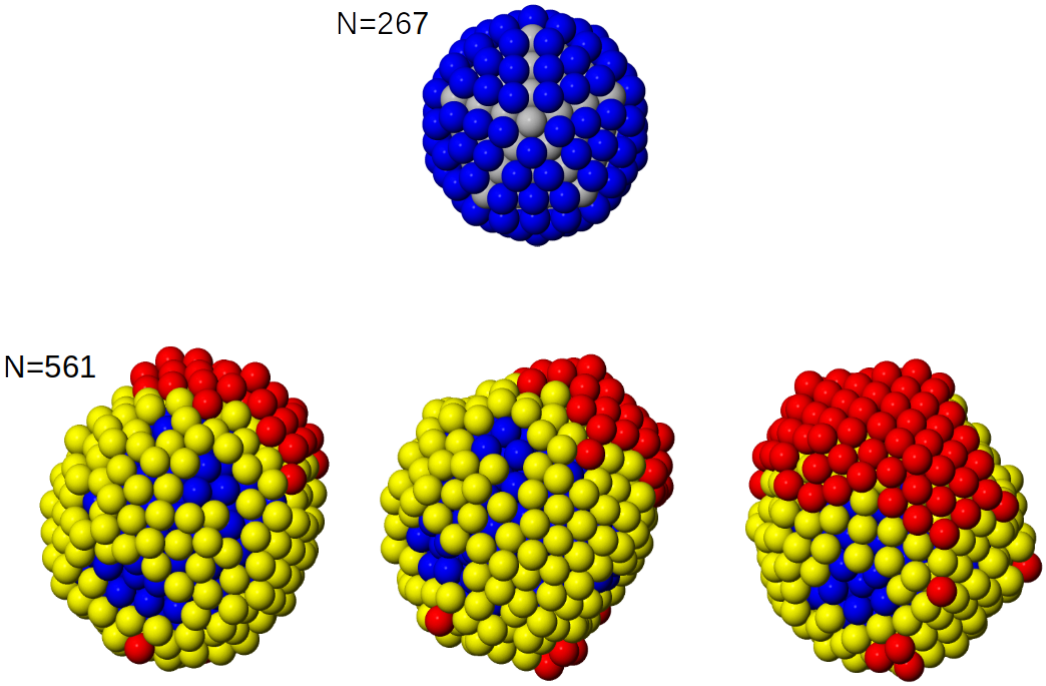

Figure S 6: Snapshots from a growth simulations starting from an anti-Mackay seed (top row) and leading to an irregular rough structure at size $N = 561$ (bottom row, the three snapshots show the same structure from different views). Temperature is 500 K and atoms are deposited with a rate of 1 atom every 10 ns. Grey spheres show the Mackay icosahedron of 147 atoms, which is covered by a first shell consisting of 20 perfect triangular islands on anti-Mackay stacking (blue atoms). These islands are not allowed to rearrange by keeping some of their atoms fixed. Yellow and red atoms belong to the second and third grown shell, respectively.

References

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