# —Supporting Information—

# Spontaneous Structure Transition in Nanoparticle Aggregates: From Amorphous Clusters to Super-crystals

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## **Materials and Methods**

#### Materials

Amphiphilic diblock copolymer polystyrene-*block*-poly(acrylic acid) ( $PS_{17}$ -*b*-PAA<sub>83</sub>,  $M_n = 1800$  for the polystyrene block and  $M_n = 6000$  for the poly(acrylic acid) block,  $M_w/M_n = 1.4$ ) and thiol-terminated polystyrene ( $PS_{115}$ -SH,  $M_n = 12000$ ;  $PS_{470}$ -SH,  $M_n = 50000$ ) were purchased from Polymer Source, Copper specimen grids (200 mesh) with formvar/carbon support film (referred to as TEM grids in the text) were purchased from XinXing BaiRui (T10023).

#### Characterization

Transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at  $100 \sim 120$  kV.

#### **Preparation of TEM Samples**

TEM grids were treated with oxygen plasma in a Harrick plasma cleaner/sterilizer for 45 s to improve the surface hydrophilicity. The hydrophilic face of the TEM grid was then placed in contact with the sample solution. A filter paper was used to wick off the excess solution on the TEM grid, which was then dried in air for 30 min.

### Assembly of Au@PS core@shell nanoparticles (NPs)

A solution of citrate-stabilized Au NPs ( $d_{Au}$  = 15.2 nm, 2 mL) was concentrated to ~ 20 µL (~ 2.9 × 10<sup>13</sup> particles/mL) by centrifugation at 16000 g for 15 min. To the deep red suspension collected at the bottom of the centrifugation tube, 1780 µL DMF was added, followed PS<sub>115</sub>-SH in DMF (7.5 µL, 8 mg/mL), PS<sub>470</sub>-SH in DMF (12.5 µL, 8 mg/mL), and PS<sub>17</sub>-*b*-PAA<sub>83</sub> in DMF (200 µL, 8 mg/mL). The mixture was then incubated at 60 °C for 2 h. After that, a small amount of water (42 µL) was added to this mixture, reducing the solubility of the PS-coated NPs. Then the mixture was incubated at 40 °C to trigger the aggregation of NPs. To monitor the structural evolution of the clusters in the growth process, 100 µL of the solution was transferred into a 1.5-mL centrifugation tube at different time. Then 1 mL of deionized water was added to the tube to induce the en-capsulation of PS-PAA on NP clusters. The resulting PS coated NP aggregates were isolated and purified by centrifugation and redispersed in deionized water and then loaded on TEM grids.

In the control experiment, 20  $\mu$ L (8 mg/mL, in DMF) of PS<sub>115</sub>-SH was used instead of the mixture of PS<sub>115</sub>-SH and PS<sub>470</sub>-SH. Other experimental conditions were kept the same.



*Figure S1*.(**a** – **d**) TEM images of the clusters obtained at the growth time of 1, 5, 15, and 60 min, respectively.



*Figure S2*. (a - b) TEM images of the super-crystals obtained at different tilt angles of the TEM grids.



*Figure S3*. TEM image of the individual Au@PS NPs coated by PS-PAA. The shell is a mixture of two kinds of PS with average molecular weight (Mn) of 12k and 50k respectively. The mole ratio between them is about 2.5 : 1. The inset shows the distribution of the shell thickness, and the average value is 8.2 nm.



*Figure S4*. Enlarged TEM images of the products obtained with only PS of 12k. All of the clusters are amorphous.



**Figure S5.** The three-dimensional (3D) structure of the icosahedral clusters can be determined by comparing their different two-dimensional (2D) patterns with the 3D models (constructed with the software Diamond 3.1. <u>http://www.crystalimpact.com/diamond/Default.htm</u>). For example, (a1 - a5) are TEM images of a cluster containing 13 NPs obtained at different tilt angles of the TEM grid. These different 2D patterns can be reproduced in viewing a 3D model of an icosahedron from different directions (b1 - b5).



Figure S6. To understand why the stability of a structure depends on the range of interaction between the building units, let us consider two 2D structures formed by solid spheres (a1 - a3). In the square structure (a2), there are four nearest pairs (contacts, indicated by the red lines) and two next-nearest pairs (indicated by blue lines), while in the rhombic structure (a3), there are five nearest pairs and no next-nearest pair. The distance between the non-contacted pair in the rhombic structure is larger than the one between the next-nearest pairs in the square structure (1.732 vs. 1.414), so we do not consider this pair. For short-range interaction, we only need to consider the interaction between the nearest pairs. As a result, the rhombic structure should be more stable than the square structure, because the former has more nearest pairs. The range of hydrophobic interaction is short, so for the building units of Au NPs coated by one kind of PS (Mn: 12k) (b1 - b3), them tends to form the structure with largest number of nearest pairs. As we mentioned in the manuscript, the icosahedral structures usually have the largest number of nearest pairs compared to other structures containing same number of building units, so they are more favorable in energy when the range of interaction is short. When we use two kind of PS (Mn: 12k and 50k, respectively) to coat the Au NPs (c1), the "apparent" range of interaction between the Au@PS NPs is extended. For example, in the square structure, the NPs on the diagonal can interact through the long-chain PS (c2) in despite of the fact that the range of hydrophobic interaction itself is still short. The contribution from the next-nearest pairs may make the square structure (c2) more stable in energy than the rhombic structure (c3). Similarly, in this case the icosahedral structures may not be the most stable one, as we observed in our experiments.



*Figure S7.* The angle between two faces of a tetrahedron is ~ 70.5 °(a), so there should be a gap of ~ 7.4 °when five tetrahedrons are put together around an axis (b). This fact indicates that if we put 7 solid spheres to form a decahedron, two of the nearest spheres will not be contacted (c). In other words, if all of the nearest spheres are contacted (d), there should be some kind of deformation of the spheres in this decahedron. The deformation exists in all icosahedral structures, which causes strain energy in them.