Electronic Supplementary Information

Polymorphism in nanoparticle-based crystals depending upon their single or polycrystalline character

Nicolas Goubet*, Pierre-Antoine Albouy, Andrew Thompson and Marie-Paule Pileni

Figure S1. Bright (a) and dark (b) field TEM pictures of the as-synthesized gold nanocrystals with their size distribution (c).
Figure S2. Optical micrograph of a capillary used to grow polyhedral superlattices.
**Figure S3.** Typical polyhedral NC superlattice made of polycrystalline gold nanocrystals that are selected for the X-ray diffraction experiments.
Figure S4. Typical polyhedral NC superlattice made of gold single crystals that are selected for the X-ray diffraction experiments.
Figure S5. Reconstruction of reciprocal space planes of equation l=0 at small q value (q_{max}=7 nm^{-1}) of one polyhedral nanocrystal superlattice made of gold single crystals.
Figure S6. Reconstruction of reciprocal space planes of equation $h+k=0$ at small q value (
$q_{\text{max}}=7 \text{ nm}\text{ }^{-1}$) of one polyhedral nanocrystal superlattice made of gold single crystals.
Figure S7. Reconstruction of reciprocal space planes of equation $h+k+l=0$ at small $q$ value ($q_{\text{max}}=7 \text{ nm}^{-1}$) of one polyhedral nanocrystal superlattice made of gold single crystals.
Figure S8. Reconstruction of reciprocal space planes of equation l=0 at small q value ($q_{\text{max}} = 7$ nm$^{-1}$) of one polyhedral nanocrystal superlattice made of gold polycrystals.
Figure S9. Reconstruction of reciprocal space planes of equation h+k=0 at small q value (q$_{\text{max}}$=7 nm$^{-1}$) of one polyhedral nanocrystal superlattice made of gold polycrystals.
Figure S10. Reconstruction of reciprocal space planes of equation h+k+l=0 at small q value ($q_{\text{max}}=7$ nm$^{-1}$) of one polyhedral nanocrystal superlattice made of gold polycrystals.
Figure S11. SAXS powder profiles for gold single (a-b) and polycrystals (c-d) with different size.
Figure S12. Reconstruction of reciprocal space planes of one polyhedral nanocrystal superlattice made of gold single crystals at 110K (a) and 290K (b).
Figure S13. The 4 possible reconstructions of reciprocal space planes of equation $h+k+l=0$ of one polyhedral nanocrystal superlattice made of gold polycrystals.
Calculation of the inorganic core density in the colloidal crystal

In the case of BCC superlattice:

\[
\Phi_{\text{bcc}} = \frac{2 \times \frac{4}{3} \times \pi \times \left(\frac{D_{\text{TEM}}}{2}\right)^3}{a_{\text{bcc}}^3} = 29.5\%
\]

where \(d_{\text{inor}}\) is the metallic NC diameter determined by TEM and \(a_{\text{bcc}}\) is the \(\text{bcc}\) unit cell.

In the case of FCC superlattice:

\[
\Phi_{\text{fcc}} = \frac{4 \times \frac{4}{3} \times \pi \times \left(\frac{D_{\text{TEM}}}{2}\right)^3}{a_{\text{fcc}}^3} = 29.5\%
\]

where \(d_{\text{inor}}\) is the metallic NC diameter determined by TEM and \(a_{\text{fcc}}\) is the \(\text{fcc}\) unit cell.