Supporting informations

Modulating Physical Properties of Isolated and Self-Assembled Nanocrystals Through Change in Nanocrystallinity

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Gold Nanocrystals synthesis.

The synthesis of Au nanocrystals was reported in a previous paper.^{1, 2} Two solutions are used to produce Au NCs. The first consists of 0.25 mmol of Chlorotriphenylphosphine Au(I) dissolved in 25 mL of toluene to which 500 μ L of dodecanthiol is added. The second one is made of 2.5 mmol tert-butylamine borane complex in 2 mL of toluene. Both solutions are placed in a silicon bath. When they reach 100°C, the two solutions are mixed together, resulting in a dark red solution which reveals the presence of gold nanocrystals. Then, the nanocrystals are precipitated and washed with ethanol and redispersed in toluene.



Figure S1. HRTEM images and related schemes showing typical morphologies of the NCs synthesized by organometallic route. The corresponding structure of these NCs is either single crystal (a, b) or multiply twinned (c, d). The scale bars represent 2 nm.

Nanocrystallinity selection.

The nanocrystallinity segregation is achieved via the simultaneous supra crystallization, which is described in our previous paper.³ Briefly, the colloidal solution is kept in a closed container and, after 7 days, a bright thin interfacial film and precipitates appear. The interfacial supracrystals can be collected with a ring like DuNouy ring and precipitated supracrystals are withdrawn from the bottom of the beaker. These supracrystals are redispersed in hexane and make a single crystalline nanocrystal solution. The remaining solution was dried and toluene evaporated. Then, the resulting black precipitated is redispersed in hexane to form the polycrystalline nanocrystal solution.



Figure S2. Scheme of the nanocrystallinity selection trough supracrystallisation process (a).^{3, 4} Conical dark field TEM images of the nanocrystals making up the interfacial (b), precipitated (d) supracrystal and remaining in the solution (c). The scale bar is 20 nm. Wide angle X-ray diffraction (e) of nanocrystals making up the interfacial (blue curve), precipitated (green curve) supracrystal and remaining in the solution (red curve). The ratio between grain size deduced with Scherrer equation and diameter deduced by TEM is 91%, 96% and 60%, respectively. Stoke and anti-Stoke low frequency Raman scattering spectra (f) of nanocrystals making up the interfacial (blue curve), precipitated (green curve) supracrystal and remaining in the solution (red curve). The spectra are obtained by using an excitation wavelength at 561 nm.



Figure S3. Diameter distribution of nanocrystals in the remaining solution (a) andmaking up the precipitated supracrystals (b). Their corresponding average diameters, deduced with Gaussian fit (red curve), are 5.2 ± 0.3 nm (a) and 5.6 ± 0.2 nm (b). The diameter measurements are performed on TEM images of over 500 nanocrystals.



Figure S4. Wide angle electron diffraction of superlattice made with Au single crystal nanocrystals (a) and polycrystalline nanocrystals (b).

Time-resolved pump-probe spectroscopy.

The experimental setup used for the pump-probe studies has been described elsewhere.⁵ It is based on a regeneratively amplified Ti:sapphire laser (Clark-MXR, Model CPA-1) producing 150-fs, 500- μ J pulses at 800 nm wavelength and 1-kHz repetition rate. A portion of this beam (the pump, with energy up to 5 μ J) is loosely focused on the sample. Another fraction of the pulse is focused in a 2-mm-thick sapphire plate to generate a broadband single-filament white-light continuum (WLC) that acts as a probe after passing through a delay line. The visible portion of the WLC, extending from 430 nm to 760 nm, is overlapped with the pump beam on the sample. The transmitted/reflected light is dispersed on an optical multichannel analyzer equipped with fast electronics, allowing single-shot recording of the probe spectrum at the full 1 kHz repetition rate. By changing the pump-probe delay τ we record 2D maps of the differential reflectivity (Δ R/R) signal as a function of probe wavelength and delay. Our setup achieves, for each probe wavelength, sensitivity down to $\approx 10^{-5}$.

AFM for nanoindentation measurement.

For each indentation, AFM images before and after indentation are recorded to check the residual mark. In practice, the loadings are not systematically uniform due to the geometry of the AFM cantilever. However, by checking the residual mark, we compare the results from the uniform loading and non-uniform loading, which show very small difference within the statistical scatter, thus the use of plate model is verified. Furthermore, we try to reduce the systematical error by increasing the number of measurements. The Young's modulus value for both single domain and polycrystalline supracrystals are calculated by a number of indentations from different loading places. Only fully covered holes are selected to perform the indentation. For each indenting place, an increasing loading force is performed and

recorded until the breaking point. Immediately after each set of measurements, the cantilever is calibrated on mica substrate to obtain the up-to-date deflection sensitivity and force constant for the elastic modulus calculation. Furthermore, we verify our methodology by measuring the Young's modulus of a reference Teflon foil sample. The AFM probe used for nanoindentation is with spring constant of 4.5 N/m.

The value of single domain supracrystal is taken in case of very slight indentation when the films still remain one piece. The latter one is obtained from the measurements of indentations on both the broken and non-broken films. In the case of broken films, the breaking point is taken for the analysis, recording the loading force and the plate displacement to make a comparison with the non-broken films. Results show that data from both cases do not have huge difference. Then, the final Young's modulus of self-assembly of polycrystalline nanoparticle is the average of all obtained data. It should be noted that the Young's modulus value of supracrystals made of polycrystalline nanoparticle is very small for a supracrystal film. However, in case of a previous study of 8nm Au supracrystal films with Young's modulus around 80 MPa, the freestanding films remained robust under indentation with even greater loading force (the indentation is also performed by AFM). Hence a much softer film is expected for supracrystals of polycrystalline nanoparticle.

For the data analysis, plate model⁶ is used to calculate the Young's modulus of single domain and polycrystalline supracrystals. In the plate model, the supracrystal film is treated as a flat circular plate with constant thickness over a circular hole. The indentation of AFM tip was modeled as a uniform load over a very small central area and the edge of the plate (the supracrystal films) is simply supported (Figure S5).



Figure S5.A schematic illustration of plate model

Then the Young's modulus could be calculated from the equation below:

$$E = \frac{3wa^2}{4\pi yt^3} (1 - v)(3 + v)$$
(1)

in which E is the Young's modulus, w is the total applied load (force), a is the radius of the plate, n is the Poisson's ratio, y is the displacement of the central point and t is the thickness of the plate. In this work, the loading force is obtained by the AFM measurements directly and displacement of the central point was calculated by:

$$y = h_p - h_i - h_r \tag{2}$$

where h_p is the displacement of the piezomotor, h_i is the indentation depth which measured by AFM profile, and h_r is the deflection of the cantilever.

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