Electronic Supplementary Information

How the coating agents of nanocrystals self-assembled in 3D superlattices control their mechanical properties?

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The measurement procedure for load-displacement curves

The nanomechanical properties of supracrystals were measured with the AFM by recording the load-displacement response of the cantilever. That is, the displacement of the cantilever is recorded while applying an external load which is first increased steadily from zero to some maximum, and then decreased from maximum back to zero, as represented schematically in Figure S1. Generally, the term “loading” is used to indicate the increasing loads, while “unloading” is used to indicate the decreasing loads. In Figure S1, the effect of the different modes of response on the unloading curves is shown. For an elastic solid, the sample deforms elastically when an external load applied to cantilever. As the applied load is removed from the cantilever, the deformation is recovered during unloading, and the material regains its original shape. As a result, the geometry of the unloading is almost completely reversible as shown in Figure S1. In the case of elastoplastic solids, the loading part of the load-displacement cycle consists of an initial elastic deformation, followed by a plastic deformation. Upon unloading, elastic deformation is recovered whereas plastic deformation is not recovered. Hence, a hysteresis occurs and the unloading part of the load-displacement data follows a different path until at zero applied load. If plastic deformation occurs, then there is a residual impression is left in the sample surface.

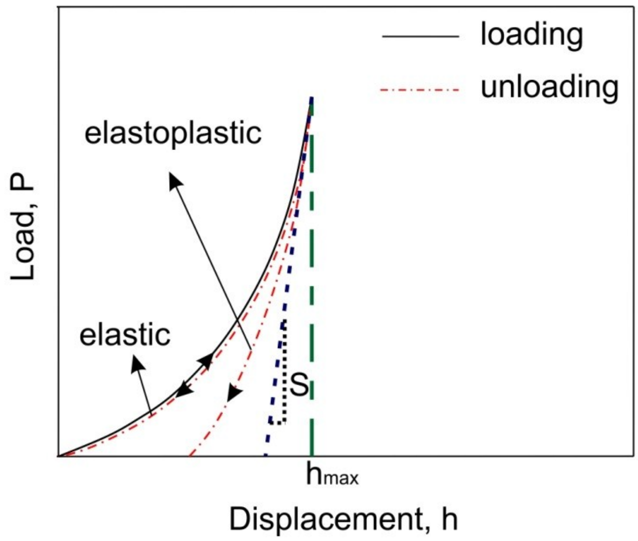

Figure S1: Schematic representation of the load-displacement curves for two nominal material responses. Here, S is the slope of the fitted line to the initial portion of the unloading curve and known as the stiffness of the material.

The measurement procedure of Young's modulus

Under displacement control, 50 to 70 indentations were made at different locations of each supracrystal by recording load-displacement curves with various applied loads and 25 nm/s displacement rate and 3 s maximum loading dwell time. To avoid substrate effects[1] the maximum indentation depth was kept to less than 10% of the supracrystal thickness, which was around 2.5 μm (Figure S4). After the indentations, the residual marks of the nanoindentations were imaged in acoustic mode of AFM.

The shape of the load-displacement curve is often found to be a rich source of information about the indented material. The Young's modulus of a material can be determined from the slope, S, of a flat line fitted to the initial portion of the unloading curve at a maximum load, together with the maximum displacement, h_{max}, for that maximum load (see Figure S1). From such a curve the Young's modulus of Ag supracrystals on silicon substrates were calculated with using Oliver and Pharr model.[2-3] Before the analysis with Oliver and Pharr model, the deflection of the cantilever, which was measured by pushing the tip over a rigid and nondeformable surface like mica, subtracted from the load-displacement curves for eliminating the contribution of cantilever deflection on measured piezo displacement.

The Oliver and Pharr analysis is based on calculating the reduced Young's modulus, E_r, with using Equation 1, where A is the values of the projected contact area of the probe, and S is the stiffness of the material, that is found by fitting a flat line to the initial part of the unloading section of the load-displacement curve.

$$E_r = \frac{S\sqrt{\pi}}{2\sqrt{A}} \qquad (1)$$

The projected area of the probe, A, depends on its profile that can be obtained by making scans over TGT1 calibration test grating (ND-MDT Co., Moscow, Russia) which is composed of an array of ultra-sharp tips.

The reduced Young's modulus, E_r, accounts for deformation of both the indenter and the sample and is given by

$$\frac{1}{E_r} = \frac{(1 - \nu^2)}{E} + \frac{(1 - \nu_i^2)}{E_i} \qquad (2)$$

where E and ν are the sample Young's modulus and Poisson's ration, respectively, and E_i and ν_i are the Young's modulus and Poisson's ratio of the indenter material, respectively. The AFM tip has a bulk Young's modulus of 130-160 GPa and a Poisson ration of $\nu = 0.27$. Because the

Poisson ratio of the supracrystals were not known, the Poisson ratio of polycrystalline bulk Ag ($\nu = 0.37$)[4] was used in the calculations.

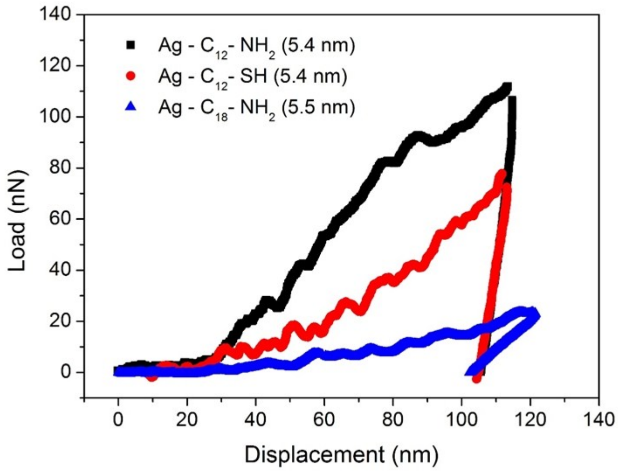

Figure S2. Comparison of load-displacement curves for different supracrystal films of 5.4-nm (or 5.5-nm) Ag nanocrystals for different coating agents.

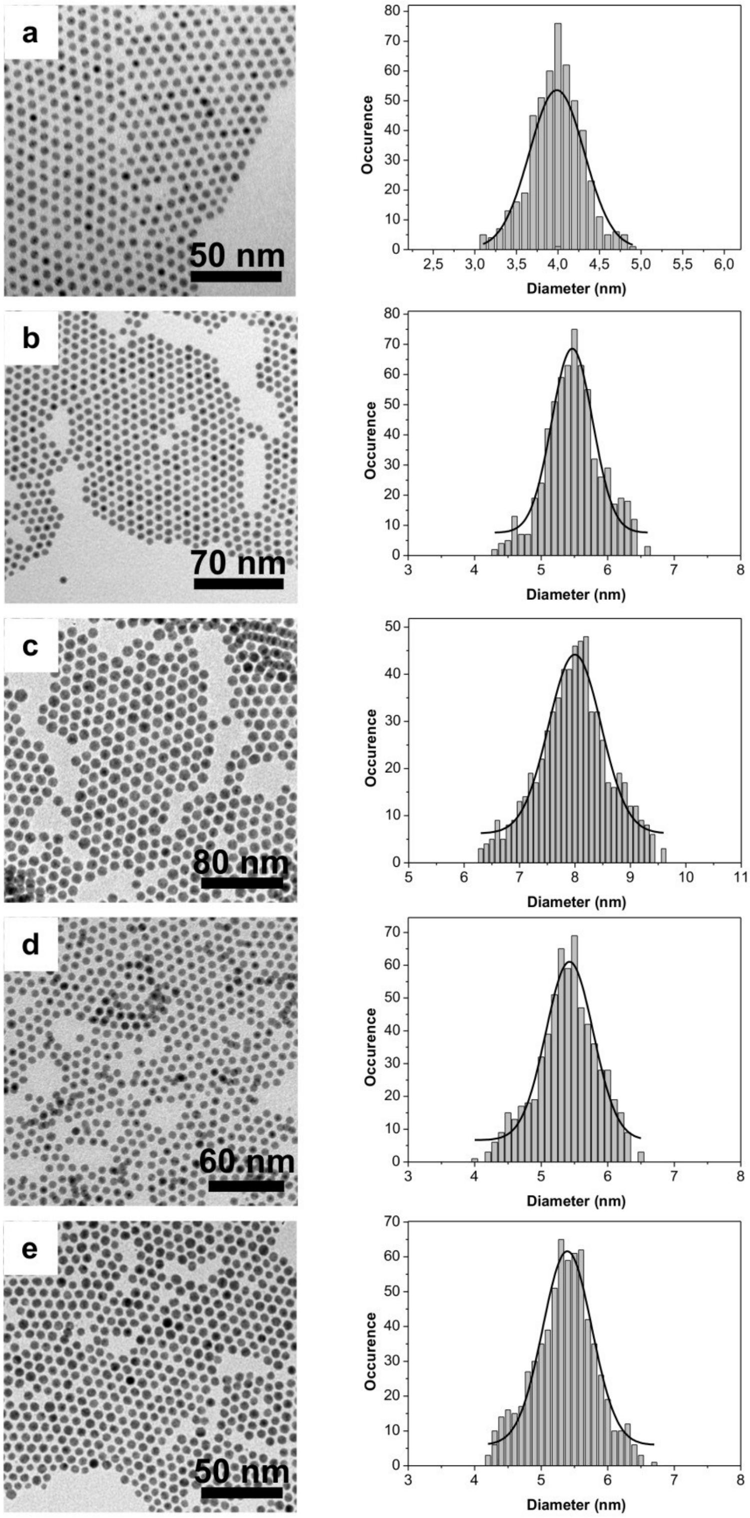
a
50 nm
Occurence
0 10 20 30 40 50 60 70 80
2,5 3,0 3,5 4,0 4,5 5,0 5,5 6,0
Diameter (nm)
b
70 nm
Occurence
0 10 20 30 40 50 60 70 80
3 4 5 6 7 8
Diameter (nm)
c
80 nm
Occurence
0 10 20 30 40 50
5 6 7 8 9 10 11
Diameter (nm)
d
60 nm
Occurence
0 10 20 30 40 50 60 70
3 4 5 6 7 8
Diameter (nm)
e
50 nm
Occurence
0 10 20 30 40 50 60 70
3 4 5 6 7 8
Diameter (nm)

Figure S3. TEM images of colloidal silver nanocrystals a) 4.0 nm coated with oleylamine, b) 5.5 nm coated with oleylamine, c) 8.0 nm coated with oleylamine, d) 5.4 nm coated with dodecylamine, e) 5.4 nm coated with dodecanethiol.

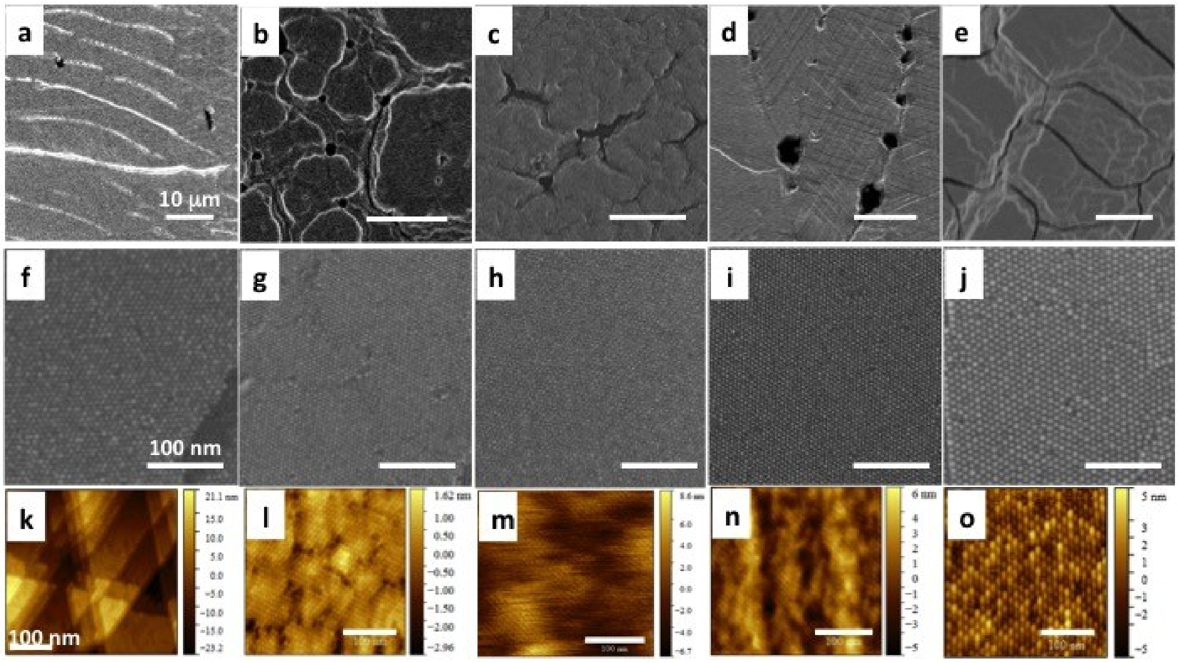

Figure S4. (a-e) SEM, (f-j) HRSEM, and (k-o) AFM images of different Ag supracrystal films deposited on silicon substrate. : (a, f, k) C_{12}-NH_2 (5.4 nm), (b, g, l) C_{12}-SH (5.4 nm), (c, h, m) C_{18}-NH_2 (4 nm), (d, i, n) C_{18}-NH_2 (5,5 nm), and (e, j, o) C_{18}-NH_2 (8 nm). The corresponding scale bar of each SEM, HRSEM, and AFM images are 10 mm, 100 nm, and 100 nm, respectively.

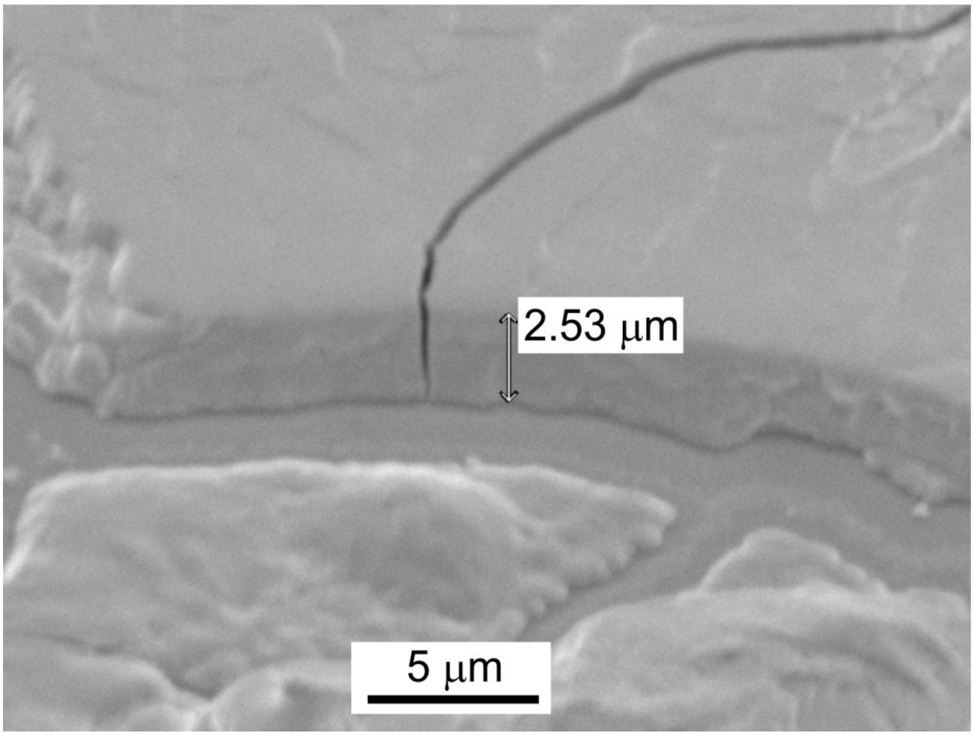

Figure S5. SEM image of supracrystals of oleylamine (C_{18}-NH_2) coated 8 nm-sized Ag nanocrystals.

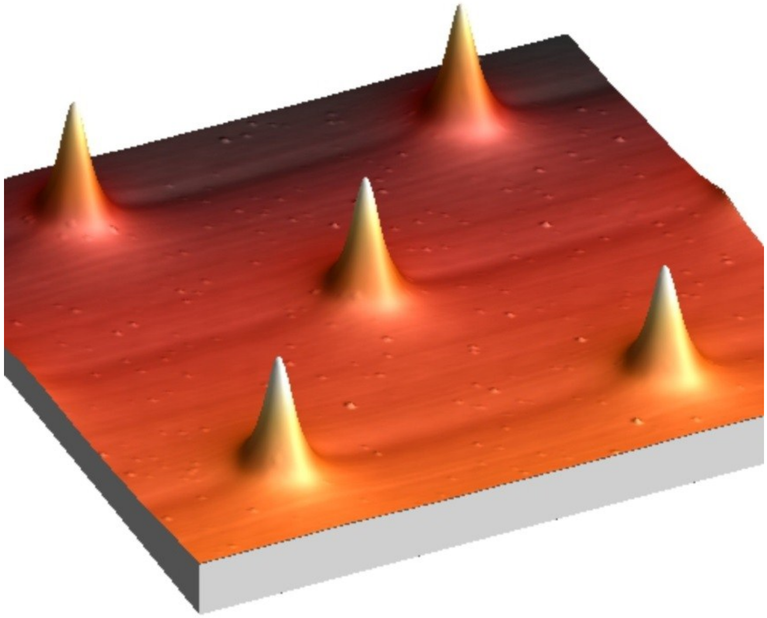

Figure S6. AFM image of TGT1 grating scanned with a sharp tip. The image dimensions 5 x 5 μm^2

References

[1] Saha, R.; Nix, W.D. Effects of the substrate on the determination of thin film mechanical properties by nanoindentation. *Acta Mater.* 2002, *50*, 23–38.

[2] Oliver, W.C.; Pharr, G.M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* 1992, *7*, 1564−1583.

[3] Oliver, W.C.; Pharr, G.M. Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology. *J. Mater. Res.* 2004, *19*, 3−20.

[4] McCarthy, E.K.; Bellew, A.T.; Sader, J.E.; Boland, J.J. Poisson's ratio of individual metal nanowires. *Nat. Comm.* 2014, *5*, 4336.