Supplementary Material (ESI) for

Seeded solution growth of nanoparticles into ordered three-dimensional supracrystals

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Materials and Methods:

NPs synthesis: Dodecanethiol (DDT)-capped gold NPs were synthesized by modifying a method reported by Zheng et al. to control the injection speed of reducing agents. The rationale for this modification is to separate nucleation from growth during particle formation. 0.25 mmol chlorotriphenylphosphine gold ($AuPPh_3Cl$) was mixed with 0.75 mmol DDT in 40 mL of benzene to form a clear solution to which 2.5 mmol of tert-butyl amine borane complex powders were then added in one portion. The mixture was stirred at 90°C for one hour, then cooled to room temperature. 100 mL of ethanol was then added to precipitate the NPs. The precipitated NPs were collected by centrifugation and washed 3 times with a mixture of benzene and ethanol. The synthesized DDT-capped AuNPs exhibit the same average mean diameter of ~ 5.5 nm with standard deviations of less than 10% (Fig. S1).

Formation of NPs monolayer films: Langmuir NPs monolayers were prepared using a Langmuir trough (type 601M, NIMA Technology). After spreading the 0.2 mg/ml NPs solution in mixed solvents of dichloromethane and hexane (vol 50:50) onto milli-Q water, the formed NPs monolayer was compressed by moving a barrier with a rate of 3 $cm^2 min^{-1}$ across the water surface. The surface pressure was measured with the Wilhelmy plate method. After compressing Langmuir monolayer films to the desired surface pressure, they were transferred to the solid substrates such as silicon wafers or silicon nitride membrane grids simply by bringing the two into contact in horizontal direction, a process known as the Langmuir-Schaefer method.

Cross-linking treatment on NP monolayer films: Cross-linking of NP monolayer films is performed in two steps: (1) cross-linking between neighboring NPs and (2) cross-linking between NPs and substrate. For (1), 5 mM ethanol solution of 1,16-hexadecanedithiol

(HDDT) was used. NP films were dipped into the cross-linking solution at room temperature for 1 hour. Subsequently, the films were removed and rinsed for 3 times with ethanol. After drying them for 5 minutes in a vacuum desiccator, the films were then annealed at 80°C for 1 hour in a nitrogen glove box. For (2), the substrate was treated with 5 mM acetone solution of (3-mercaptopropyl) trimethoxysilane. The samples were dipped into the solution at room temperature for 5 hours. Then, the samples were removed, rinsed, and dried in the way described above.

Overlayer growth of NPs on the cross-linked NP monolayer films: The overgrowth of NPs on the cross-linked NP substrates was carried out by evaporating solvent from a NP solution. For this, substrate was placed inside a glass vial and NP solution (1 ml, ~ 10^{15} NP/ml) was then added into the vial. Here, toluene, hexane, and chloroform were used as solvents. The solutions were evaporated in a vacuum chamber (Ted Pella) with controlled pressure ranging from 1 to 3 kPa and temperature from RT to 90°C over the course of 1-2 days. Subsequently, the sample was removed and rinsed with ethanol for 3 times to remove the organic residues, and then dried in a vacuum desiccator for 5 minutes.

Figure S1. Transmission electron microscopy image of the synthesized DDT-capped AuNPs.

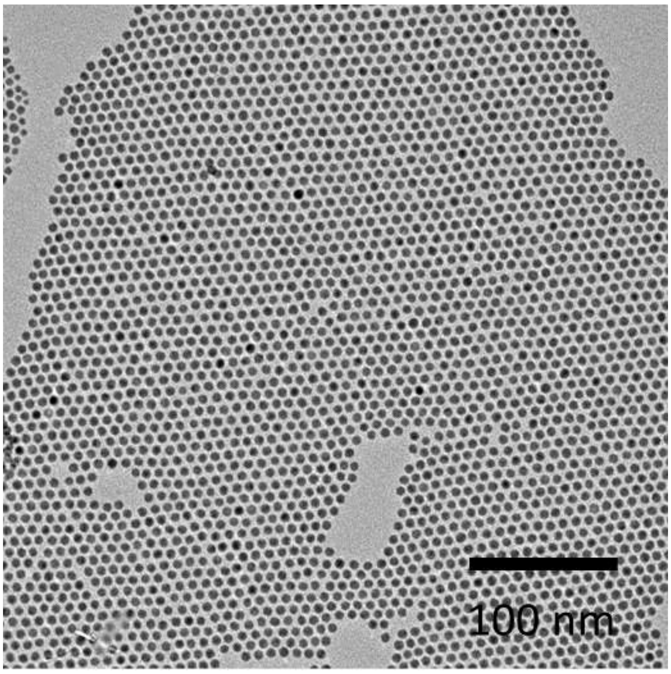

Figure S2. Effect of linker length of alkanedithiol in cross-linking process; (a) nonanedithiol, (b) hexadecanedithiol. Scale bar : 100 nm.

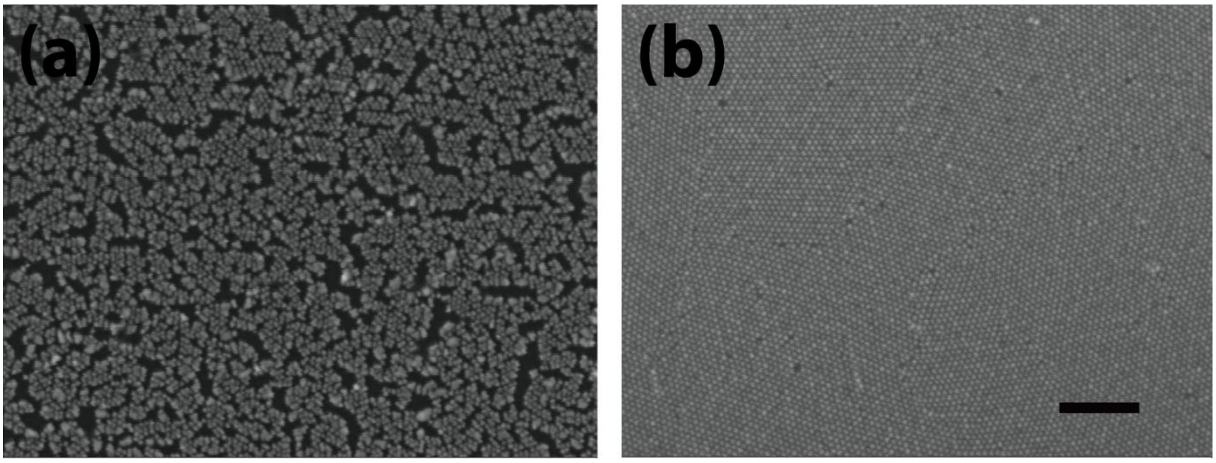

Figure S3. Stability test of cross-linked 2D NPSCs under various good solvents; (a) chloroform, (b) hexane / dichloromethane (50:50 v/v), and (c) toluene.

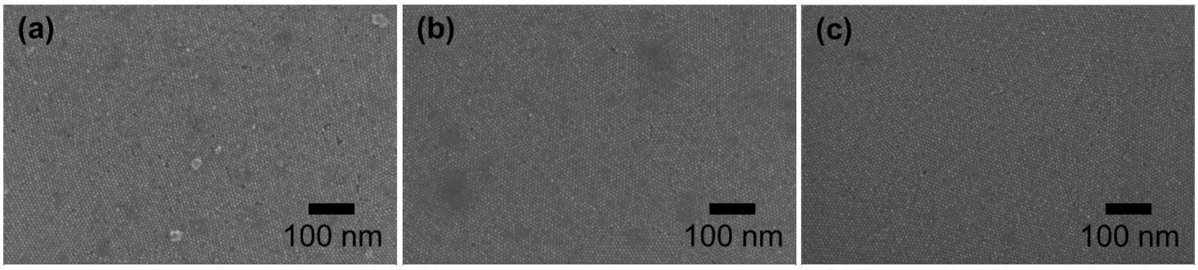

Figure S4. Growth control for 3D NPSC; effect of 2D NPSC seed.
SEM images of NPSCs structure on (a) bare substrate and (b) NPSCs substrate.

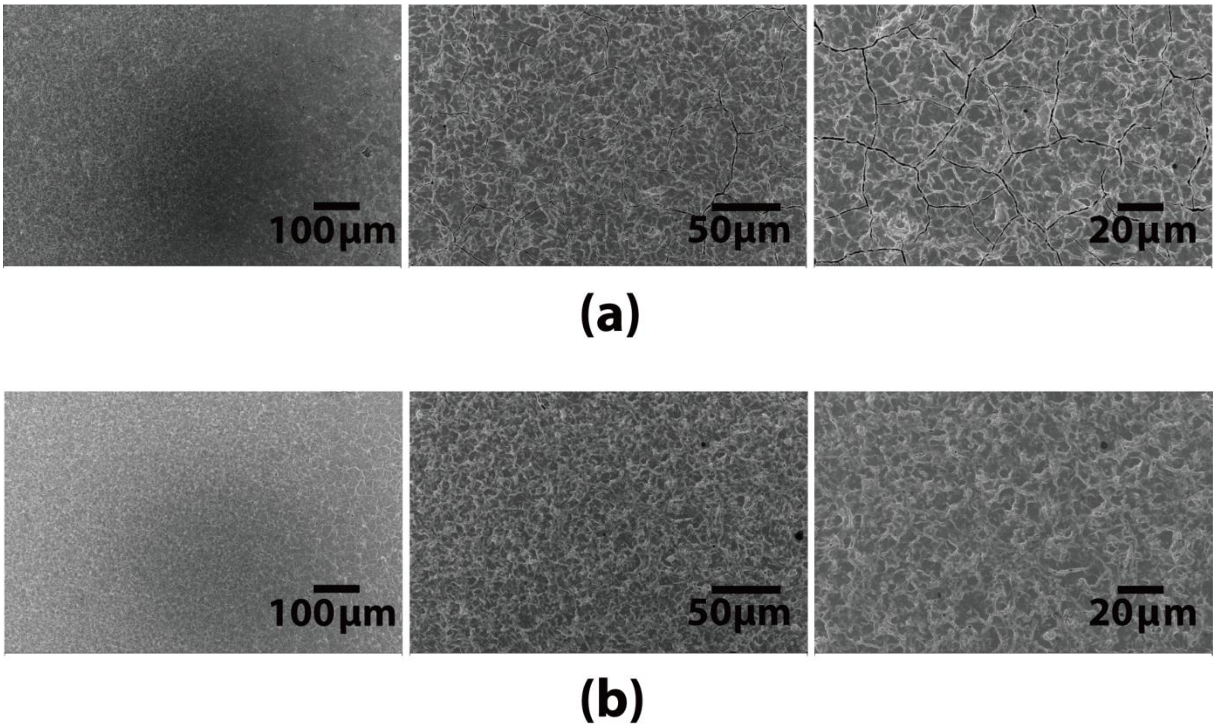

Figure S5. Growth control for 3D NPSC growth; evaporation rate.
SEM images of 3D NPSC structures grown on 2D NPSC with different evaporation rate under (a) 3 kPa and (b) 10 kPa.

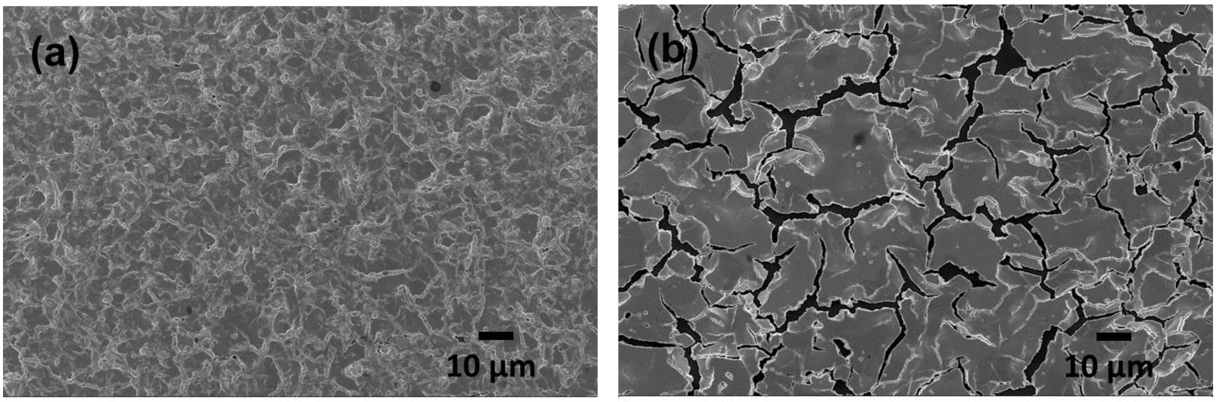

Figure S6. Growth control for 3D NPSC growth; growth temperature.
Thickness vs roughness for NPs structure as a function of growth temperature.

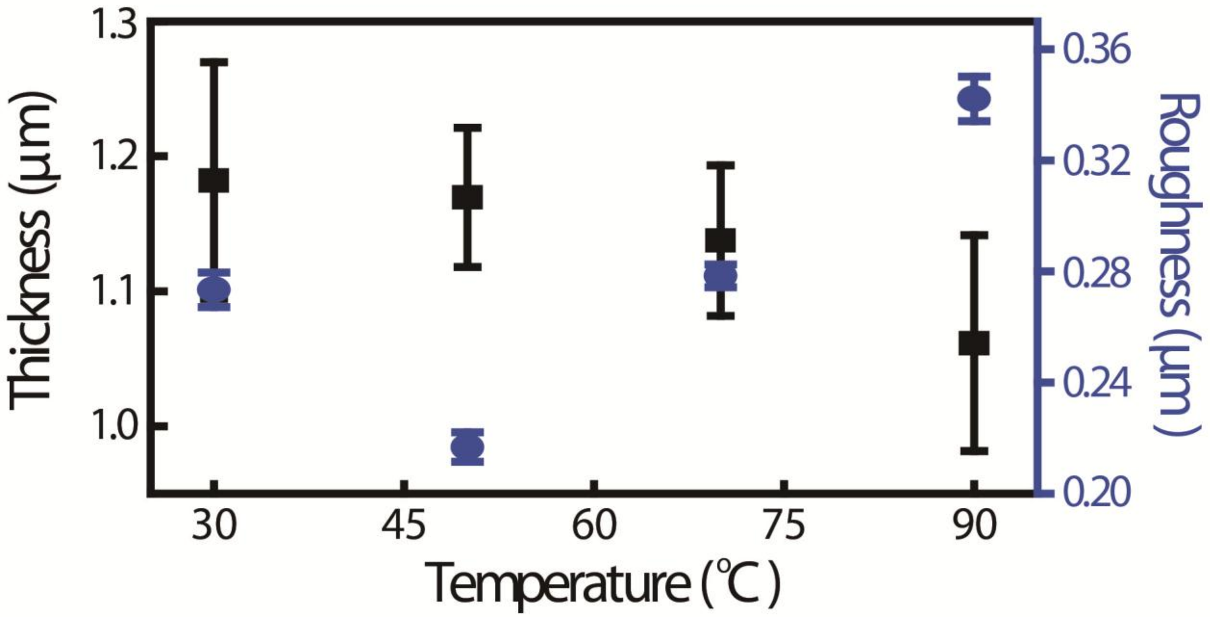

Figure S7. Growth control for 3D NPSC growth; deposition method.
SEM images of NPs structures grown by mild destabilization method on 2D NPSCs (a,b). Schematic outline illustrating the concept of the mild destabilization procedure. A buffer layer of propan-2-ol (IPA) slows down the diffusion of non-solvent (ethanol) to diffuse into a NPs solution.

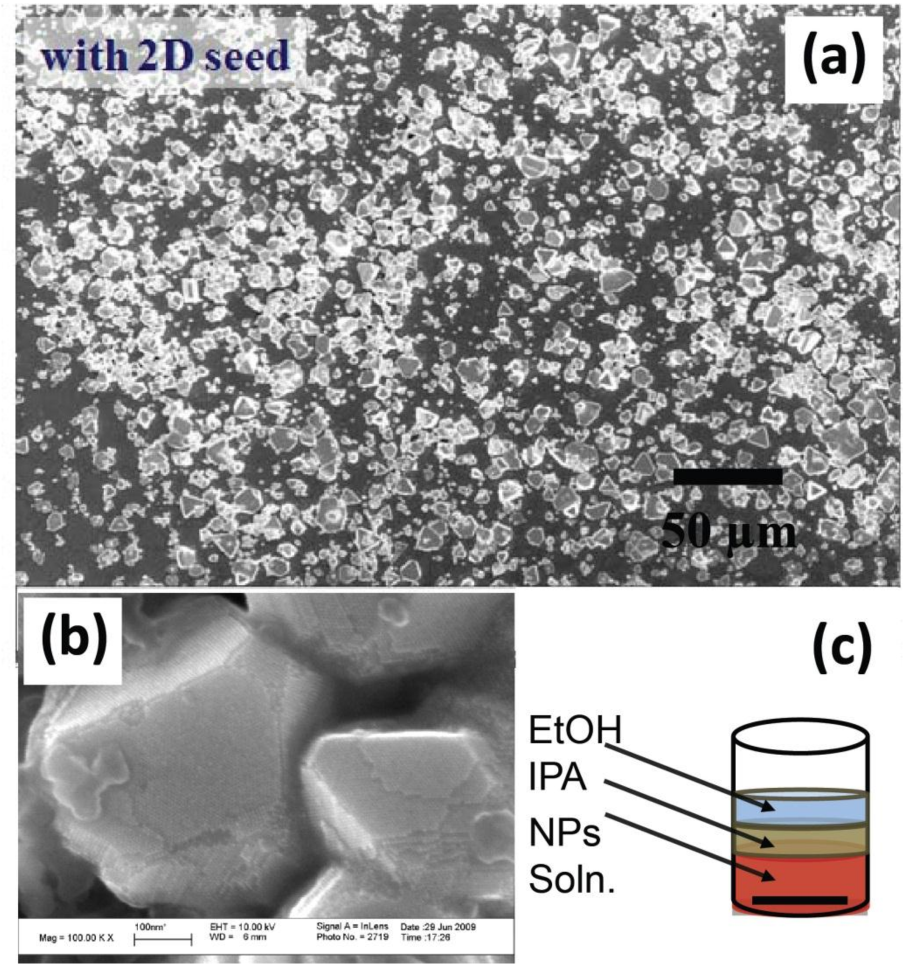

Table S1. Cross-linking of 2D NPSCs: change of the maximum peak position for 2D NPSCs cross-linked with different procedures under a stability tes^{t} consisting of immersion of the sample in toluene for 1 day at 50°C.

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Procedure*	Maximum peak position (nm) before toluene immersion	Maximum peak position (nm) after toluene immersion
(1) (c) → (a) → (b) → (d)	577	570.5 ± 0.7
(2) (a) → (b) → (c) → (d)	577	577
(3) (a) → (c) → (b) → (d)	577	568 ± 2.8

*(a) Deposition of 2D NPSC on substrate, (b) treatment with (3-mercaptopropyl)trimethoxysilane, (c) treatment with hexadecanedithiol, and (d) heat treatment at 80°C for 1 hour.

RFERENCES

(1) G. L. Gaines, in *Insoluble Monolayers at Liquid-Gas Interfaces*, Interscience Publishers: New York **1966**.