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A very large two-dimensional superlattice domain of monodisperse gold nanoparticles by self-assembly†

Sang-Kee Eah*

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We report a very large 2D superlattice domain of hexagonal close-packed monodisperse gold nanoparticles, which is longer than 20 μm and of 8.8 nm superlattice constant in a millimetre-scale monolayer film, fabricated by simple self-assembly of drying water and toluene droplets with 2D nanoparticles at the air–liquid interfaces.

Fabrication of ordered nanostructures with sub-10 nm features is important for both basic scientific study and practical applications but still remains as a big challenge. Top-down methods such as electron beam lithography do not have resolution better than 10 nm, while most bottom-up self-assembly methods have issues in fabricating uniform nanostructures on a macroscopically large area. Recent developments in synthesis of monodisperse colloidal nanoparticles have resulted in diverse self-assembled, 3-dimensional periodic ordered arrays (3D superlattices) of nanoparticles.^{1,2} While very large [$>200 \mu\text{m}^2$ or $(>50 \mu\text{m})^{3,4}$] single crystalline 3D superlattices of small ($<10 \text{ nm}$) nanoparticles were reported, the size of 2-dimensional single crystalline superlattices (2D superlattice domains) of sub-10 nm nanoparticles has remained below 1 μm with just a few recent exceptions of $>1 \mu\text{m}$,⁵ $>2 \mu\text{m}$,⁶ and $>10 \mu\text{m}$,⁷ all on top of a very slowly evaporating film of excess ligands.^{5–8} Here we, for the first time, present a 2D superlattice domain of gold nanoparticles, which is larger than 20 μm , having a spatial period (lattice constant) of 8.8 nm without using excess ligands.

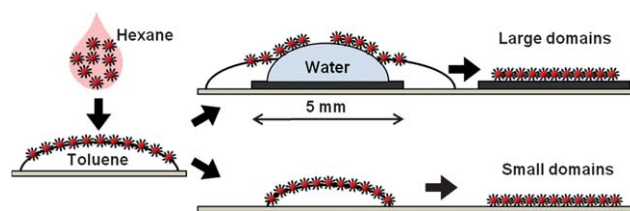
Dodecanethiolate-protected gold nanoparticles were made in $<10 \text{ min}$ using our recently reported method.⁹ Then, the diameter was increased from 3 to 7 nm by aggregation of small nanoparticles into larger ones^{4,10} in a neat dodecanethiol (DDT) solution at its boiling point of $\sim 260 \text{ }^\circ\text{C}$ for 35 min. Excess thiols were removed as much as possible by precipitating nanoparticles with methanol/ethanol and removing the thiol-containing supernatant at least 3 times, which may be a size filtering step by not collecting smaller nanoparticles in the supernatant.¹¹ The cleaned and precipitated nanoparticles were redispersed in hexane. Both the small and large nanoparticles before

and after heating in neat DDT had the special 2D self-assembly property of floating to the air–toluene interface of a toluene droplet regardless of the amount of excess thiols.¹²

A monolayer film of close-packed gold nanoparticles can be fabricated simply by drying a toluene droplet of any size, even covering the whole surface of a 3 inch silicon wafer.¹² However, the 2D superlattice domain size is smaller than 1 μm .⁹ Therefore, to increase the domain size, we transferred a monolayer film of nanoparticles from the air–toluene interface to the air–water interface of a water droplet and its surrounding toluene droplet,¹³ as shown in Scheme 1 (details in the ESI†).

Individual gold nanoparticles in the 2D liquid-like state at the air–toluene interface seem to near-freely move around, when the evaporating toluene droplet is still large enough for some inter-nanoparticle space.⁹ In contrast, we observed the 7 nm gold nanoparticles were in the 2D solid-like state at the air–water interface. By real-time, micrometre-scale optical microscopy of the surface of a drying water droplet, fragmented plates, intentionally broken from a large 2D plate of nanoparticles, were observed to move like solid objects (Fig. S2 in the ESI†). In addition, the color of the gold nanoparticle monolayer film was red-purple at the air–toluene interface and blue-purple at the air–water interface, indicating close-packing at the air–water interface (Fig. S1 in the ESI†).

A hexane droplet with gold nanoparticles was dropped onto a larger toluene droplet and nanoparticles immediately floated to the air–toluene interface. Then, the toluene droplet was pushed to surround a nearby water droplet on a $5 \times 5 \text{ mm}^2$ silicon chip. A monolayer film of the nanoparticle was deposited onto the silicon substrate after evaporation of toluene first and water later in $\sim 10 \text{ min}$ total under ambient conditions. A scanning electron microscope (SEM) was used to characterize 2D nanoparticles, after the focused



Scheme 1 Very large 2D superlattice domains are formed during transfer of a nanoparticle monolayer film from the air–toluene interface to the air–water interface of toluene and water droplets.

Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York, 12180, USA. E-mail: SangKeeEah@gmail.com; Fax: +1-518-276-6680; Tel: +1-518-276-3972

† Electronic supplementary information (ESI) available: Details of 2D self-assembly, a real-time movie, and the whole image (19 500 \times 2037 pixels, 33 Mbyte) of the 2D superlattice domain of 18 μm length with spatially resolved, 360 000 individual nanoparticles in Fig. 1D. See DOI: 10.1039/c1jm11671a

electron beam diameter is minimized below 2 nm by resolving individual nanoparticles.

Fig. 1 shows SEM micrographs of 2D nanoparticles at 4 magnifications of 45, 2k, 12k, and 200k times. By SEM, the nanoparticle layers among 0, 1, and multiple can be resolved at all length scales of nanometre, micrometre, and millimetre. At 45-time magnification ($\times 45$, Fig. 1F), multilayer areas at the edge of the water droplet's

position are white and the surrounding 0-layer areas are black. At $\times 2k$ (Fig. 1E), the central area is 1-layer thick but black due to carbon deposition after electron scanning at $\times 12k$ (Fig. 1D), while the multilayered wrinkles are white and other 1-layer areas are gray. To demonstrate that the central 2D superlattice domain surrounded by other domains at $\times 12k$ (Fig. 1D) is indeed single crystalline, we obtained 11 images at $\times 200k$ (Fig. 1A–C). Then, using single

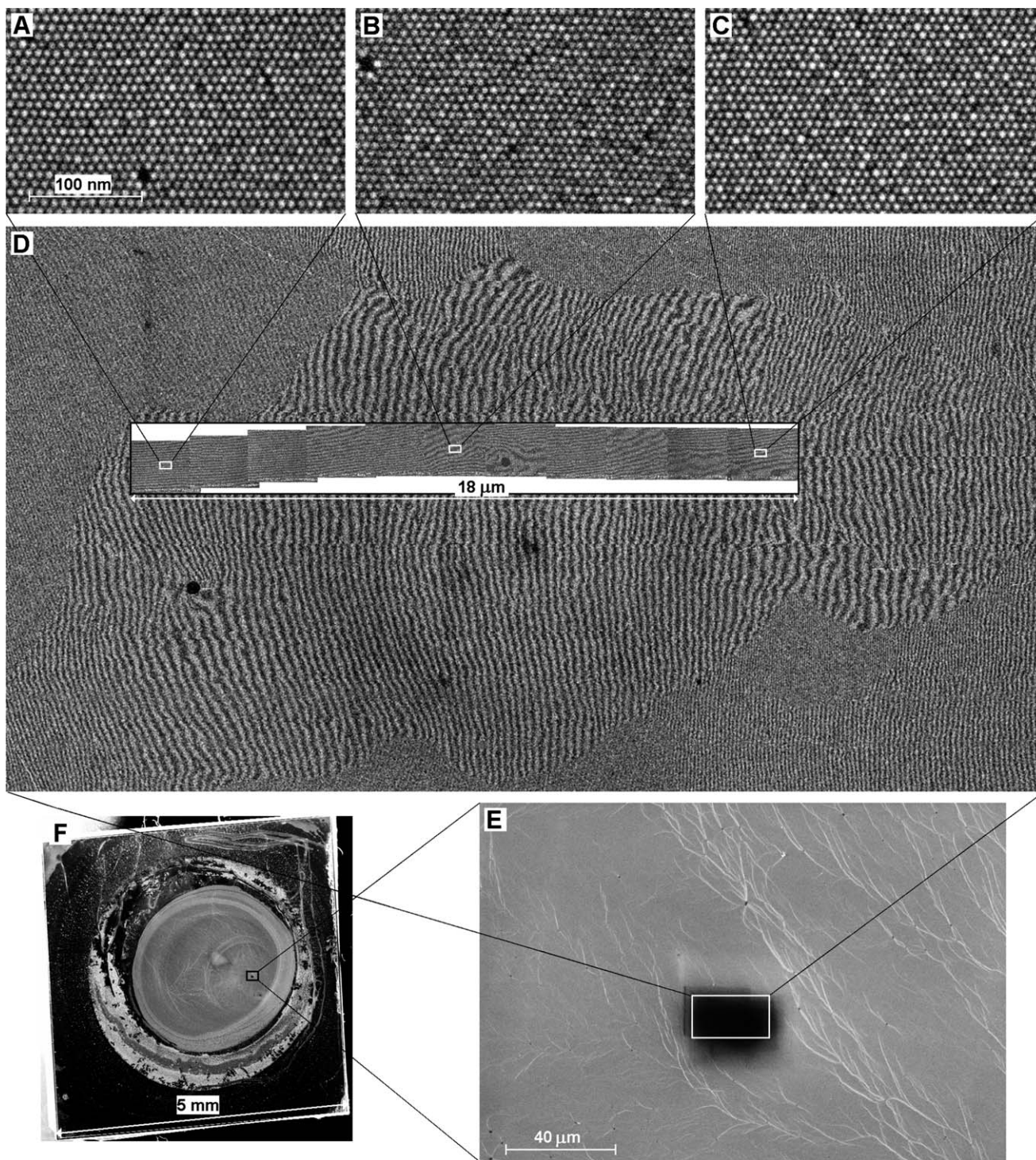


Fig. 1 SEM micrographs of a macroscopically large, millimetre-scale monolayer film of hexagonal close-packed gold nanoparticles at different magnifications with a 2D superlattice domain, longer than 20 μm and of 8.8 nm superlattice constant (common scale bar for A, B and C).

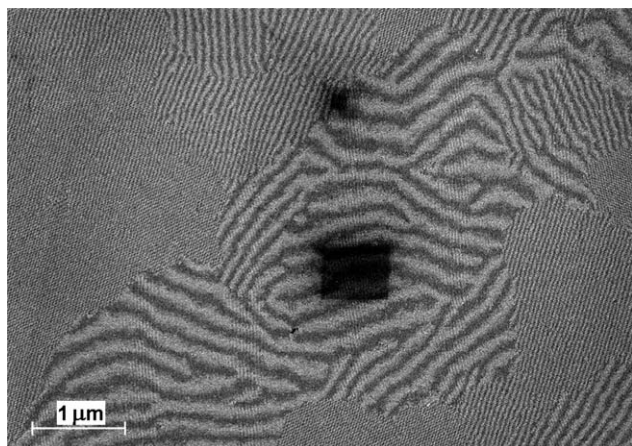


Fig. 2 2D superlattice domain boundaries by Moiré patterns at a low magnification without resolving individual nanoparticles.

vacancies as markers, we combined them into one whole image (available in the ESI†) where one of the 3 hexagonal superlattice axes is continuously horizontal from the left end to the other. There are various defects in the 2D superlattice domain: for example, a ~ 300 nm void hole with no nanoparticles, single vacancies, dislocations, one or two-nanoparticle wide lines of bilayer, and defects due to protrusions of the silicon substrate.¹⁴

2D superlattice domain boundaries can be imaged and searched using Moiré interference patterns at specific low magnifications without resolving individual nanoparticles. As the SEM magnification is varied, the scanning range changes accordingly but the focused electron beam diameter below 2 nm does not. Moiré patterns in Fig. 2 by a different batch from Fig. 1 are of higher contrast in a smaller area, since the ratio of one image pixel to the superlattice constant is 1, smaller than 3 in a larger area of Fig. 1D. We have learned that Moiré fringe intervals and orientations were different among neighboring domains, due to not varying superlattice constants but different hexagonal superlattice orientations.

Gold nanoparticles of 5 nm diameter without heating in neat DDT were synthesized with a precisely known amount of DDT molecules, 10% of gold atoms without any need for post-synthesis cleaning.⁹ However, the size uniformity was not high enough for 2D superlattice domains >10 μm . Gold nanoparticles of 7 nm diameter after heating in neat DDT were more uniform in size and large 2D superlattice domains were formed, though post-synthesis cleaning was required and the amount of excess DDT ligands could not be precisely quantified. We discovered that a critical factor is not the amount of excess DDT ligands but delicately controlling the convective flow of nanoparticles. For example, several batches of self-assembly using the same batch of synthesized gold nanoparticles generated different 2D superlattice domain sizes. In a millimetre-scale silicon chip, the largest domain was found after a time-consuming search even with micrometre-scale Moiré patterns. How can we further increase the largest domain size, for example >100 μm : an “annealing” process,¹⁵ controlling nanoparticles between 2D liquid and solid states and/or better controlling the convective flow¹⁶ of nanoparticles from the air–toluene interface to the air–water interface, like in a vacuum chamber? The air–water interface might be replaced by the air–

diethylene glycol interface,¹⁷ where a 2D superlattice domain >3 μm and of 17 nm superlattice constant was recently reported.¹⁸

In conclusion, we fabricated a macroscopically large, millimetre-scale monolayer film of hexagonal close-packed monodisperse gold nanoparticles with a 2D superlattice domain larger than 20 μm and of 8.8 nm superlattice constant, which is the largest and first reported one to the best of our knowledge. Very large 2D superlattice domains are formed during convective flow transfer of a nanoparticle monolayer film from the air–toluene interface in the 2D liquid-like state to the air–water interface in the 2D solid-like state using a water droplet surrounded by a toluene droplet, which can be deposited onto any substrate after evaporation of liquid droplets without using any sophisticated instruments.

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Very large two-dimensional superlattice domain of monodisperse gold nanoparticles by self-assembly

Sang-Kee Eah

Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute
Troy, New York 12180, USA, E-mail: SangKeeEah@gmail.com

Details of the 2D self-assembly process

As shown in Fig. S1, gold nanoparticles with a special property for 2D self-assembly float to the air-toluene interface of a toluene droplet and form a monolayer film. The floating is immediate if the toluene droplet is larger than the hexane droplet initially containing gold nanoparticles (Scheme 1 in the main text) and slower if the hexane droplet is of size similar to or larger than the toluene droplet [1]. Hexane evaporates ~ 4 times faster than toluene. A nearby water droplet is pushed to the toluene droplet that surrounds it. Then, gold nanoparticles are transferred from the air-toluene interface to the air-water interface. The color of the gold nanoparticle monolayer film is red-purple at the air-toluene interface and gold nanoparticles might be in the 2D liquid state, meaning that nanoparticles are not close-packed and there are some thermal movements of individual nanoparticles at the 2D interface between air and toluene. In contrast, the color is blue-purple at the air-water interface, meaning close-packed gold nanoparticles that might be in the 2D solid state. Fragmented 2D plates of gold nanoparticles in Fig. S2 further support the hypothesis of the 2D solid state at the air-water interface. While individual microspheres can be spatially resolved in real-time by optical microscopy for phase transition between 2D liquid and solid [2], no electron or X-ray microscopy is yet available for resolving individual nanoparticles' thermal motions at the air-liquid interface of a liquid droplet. Instead, we plan to do some grazing-incidence small angle X-ray scattering (GISAXS) experiments to verify the 2D liquid or solid states of gold nanoparticles at the air-liquid interfaces. For scanning electron microscopy of gold nanoparticle superlattice domains, we put a water droplet on a silicon piece of $5 \times 5 \text{ mm}^2$ area, a toluene droplet around the water droplet, and a hexane droplet with gold nanoparticles in it. After evaporation of hexane, toluene, and water in this order, the monolayer film of gold nanoparticles is very gently deposited onto the silicon substrate.

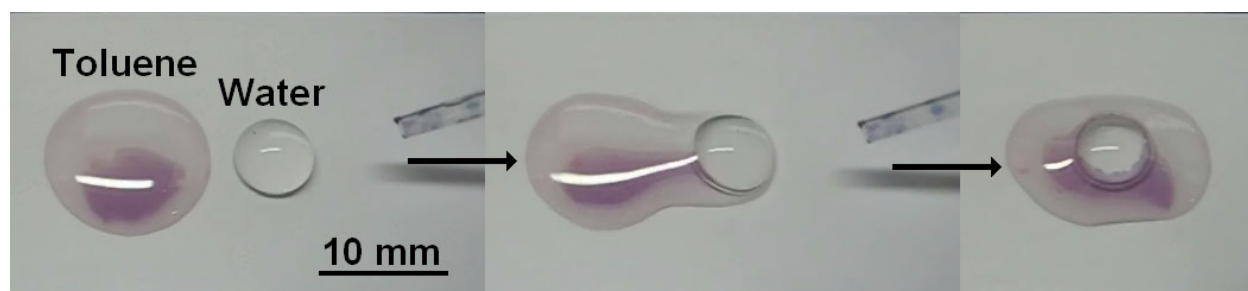


Fig. 1S Gold nanoparticles of red-purple color and in 2D liquid-like state at the air-toluene interface are transferred to the air-water interface where they are of blue-purple color and in 2D solid-like state (images taken from a real-time movie).

Electronic Supplementary Information, <http://dx.doi.org/10.1039/C1JM11671A>

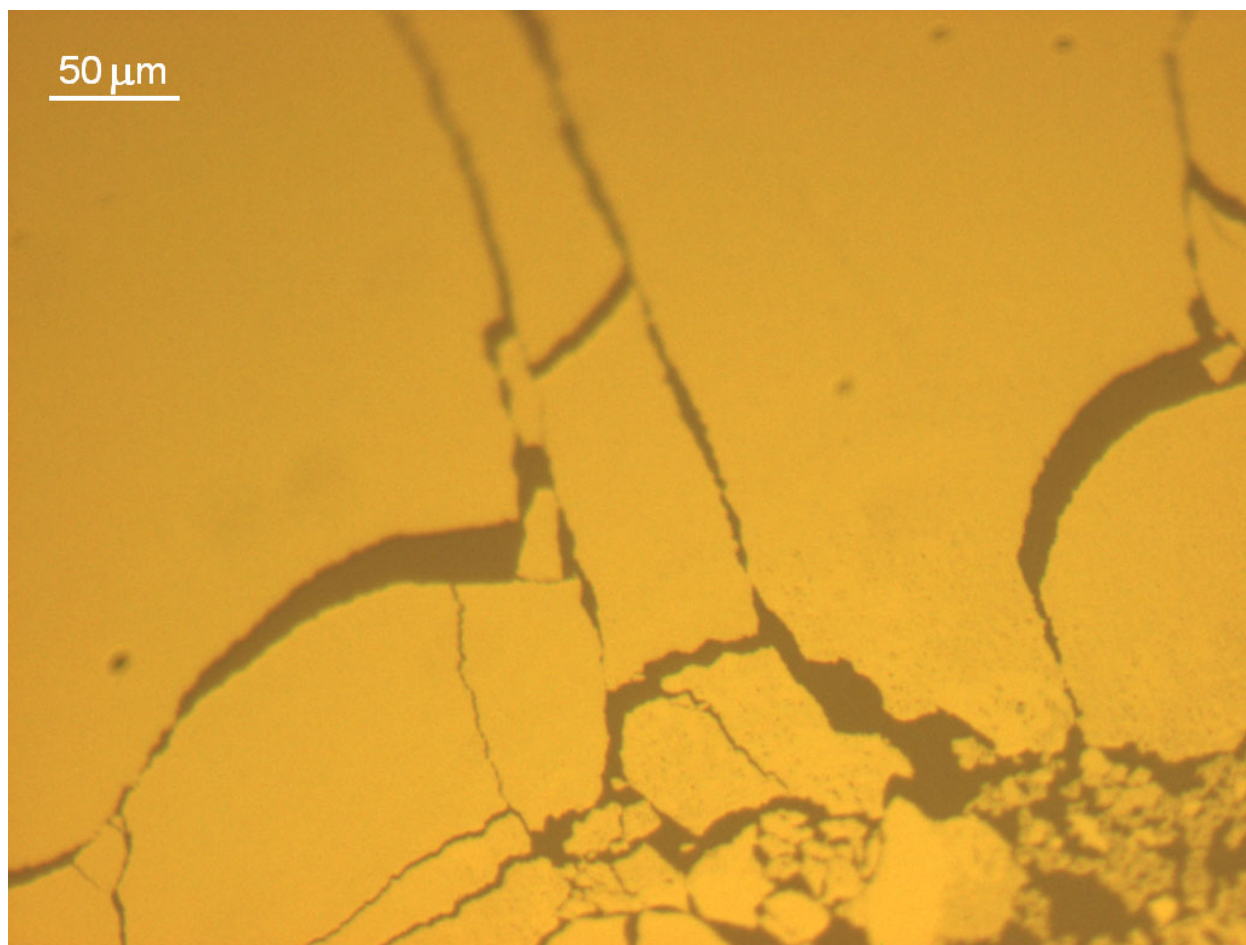


Fig. 2S Fragmented 2D plates of gold nanoparticles at the air-water interface.

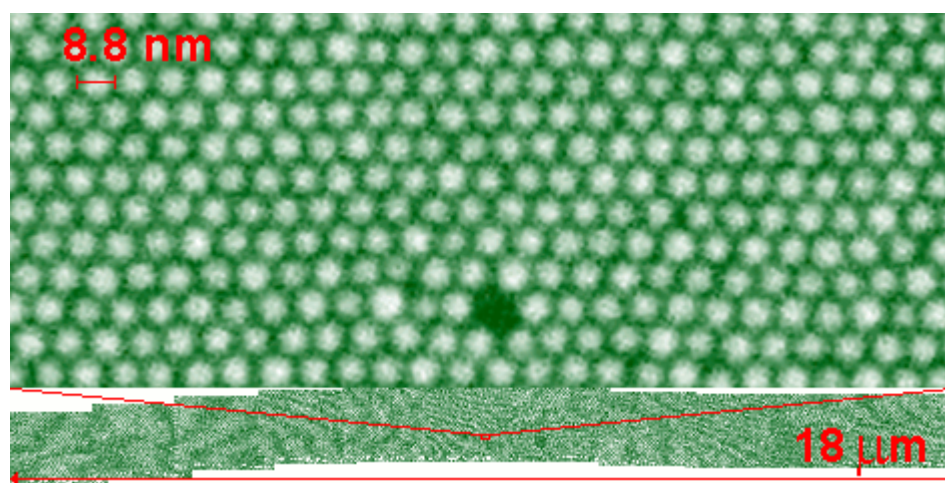


Fig. 3S Whole SEM image of the 2D superlattice domain with spatially resolved individual gold nanoparticles and defects such as single vacancy and dislocation, available as ESI to be downloaded (19500 x 2037 pixels, 33 Mbyte).

Electronic Supplementary Information, <http://dx.doi.org/10.1039/C1JM11671A>

Movie of Fig. 1S and the whole image of gold nanoparticles in Fig. 1d

Fig. 1S are images taken from a real-time movie (4.5 Mbyte, mpg format) that is also available as ESI in addition to the whole SEM image (19500 x 2037 pixels, 33 Mbyte, gif format) of the 2D superlattice domain of 18 μm long with spatially resolved, 360,000 individual nanoparticles and defects such as single vacancy and dislocation (Fig. 3S). If the ESI gif image file (33 Mbyte) is so large that there are some difficulties in downloading and watching it, a 7-min video for zooming into and panning the huge image is available at YouTube (search keyword: EahLab, "<http://www.youtube.com/watch?v=vLudYhwXyAM>").

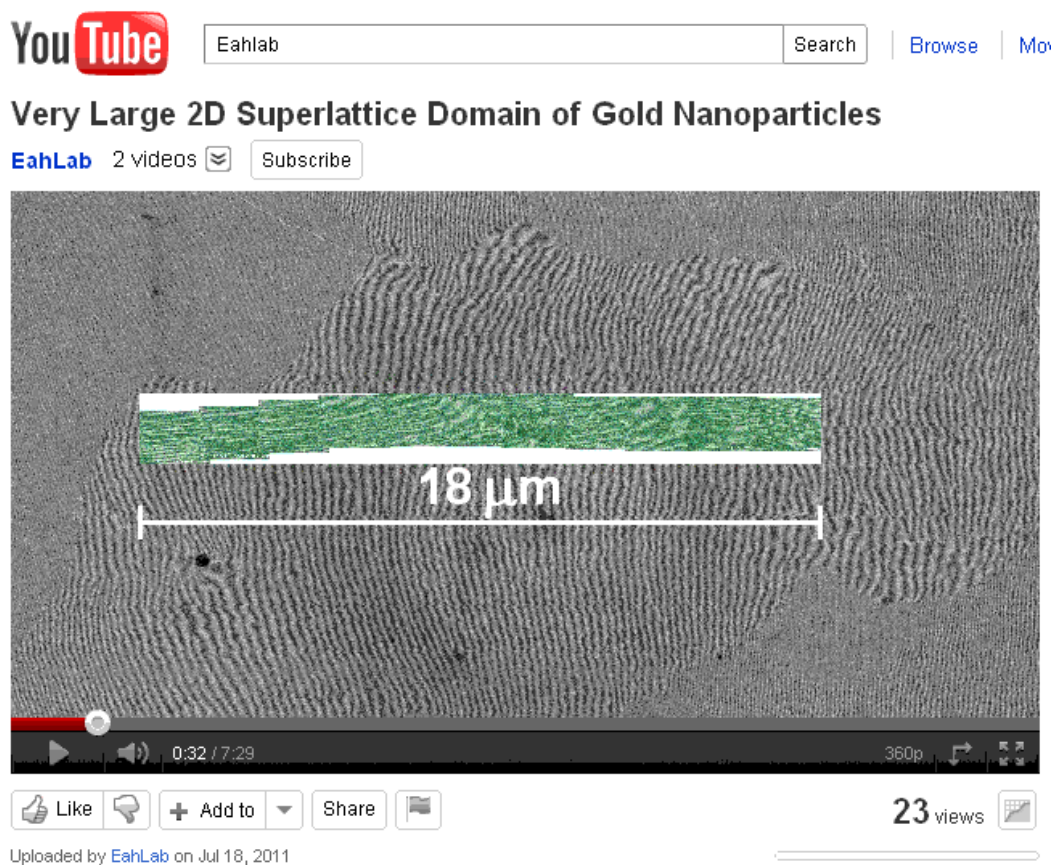


Fig. 4S 7-min video for zooming into and panning the huge image in Fig. 3S, available at YouTube (search keyword: EahLab, "<http://www.youtube.com/watch?v=vLudYhwXyAM>").

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