

Supporting Information

Temperature dependence on charge transport behavior of three-dimensional superlattice crystals

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Supporting Information (SI) 1

(A) Synthesis of mercaptosuccinic-acid monolayer-protected gold nanoparticles

(Au-MSA NPs): Au-MSA NPs having average core sizes of ~ 2 and ~ 4 nm were synthesized by our established methodology.¹⁻⁵ Briefly, 4.12 mL (5%) of aq. HAuCl₄ was mixed with 100 mL of methanol (99.8%). This was then immersed in an ice bath having provisions for vigorous stirring and sonication. 150 mg of MSA was then added to the mixture with stirring and sonication upon which a clear yellow solution results. To this mixture, NaBH₄ solution (190 mg in 20 mL water) was added drop-wise (at the rate of 120 mL/h). The solution becomes brownish black after the addition of NaBH₄. Stirring and sonication were continued for nearly 30 min after the addition of NaBH₄ under the ice bath temperature. The solution containing the NPs was then agitated with Ar for 90 min. This was then kept for aging for a day. The monolayer-protected NPs were separated by centrifuging at 10,000 rpm for 7 min. The separated Au MSA-NPs were

washed with methanol-water mixture (30% (v/v)) three times and finally once with methanol and ethanol, respectively. The washed precipitate was dried in rotavapor. The dried precipitate was then dissolved in a minimum amount of Millipore water and subjected to dialysis against fresh distilled water for 24 h to remove surface bound impurities, if any, such as Na^+ , free thiols, etc. The dialyzed material was then freeze dried. The Au:S mole ratio in the above synthesis was 1:2 and the average size of the NP cores as estimated from transmission electron microscopy was ~ 2 nm. The average size of the cluster cores was increased to ~ 4 nm by varying the Au:S mole ratio to 1:1 in the above procedure.

(B) Fabrication of three-dimensional superlattice crystals (3-D SLs) of Au-MSA at the air-water interface: 3-D SLs were fabricated at the air-water interface by our well-established procedures.²⁻⁵ 3-D SLs with average cluster core sizes of 4 nm were synthesized from the ~ 2 nm Au-MSA NPs by direct acidification with HCl. Briefly, 6 mg of the freeze dried Au-MSA NPs was dissolved in 1.9 mL of Millipore water. 100 μL of HCl (6 M) was then added to the mixture, followed by filtering the same using a syringe driven filter (0.2 μm pore size). The acidified solution put in a clean bottle was then kept in a dark and vibration free environment. 3-D SLs appear at the air-water interface as a golden yellow film after about 5 days. Synthesis was done in multiples to get enough materials of 3-D SLs.

3-D SLs with the average core sizes of 6.2 nm was prepared from the as-prepared Au-MSA NPs (~ 4 nm size synthesized using the 1:1 Au:S mole ratio) by the same methodology. However, for getting the 3-D SLs with core sizes of 7.5 nm size, we have

used the vapor diffusion method recently reported.⁶ The Au-MSA NPs (~ 4 nm size), first filtered through a filter-driven syringe, was poured into a clean bottle. 6 M HCl was taken in another bottle of the same size. Both the bottles were placed in another bottle and then the mouth of the outer bottle was covered. This facilitates slow diffusion of HCl vapors into the Au-MSA solution, which creates very few crystallization centers and therefore crystals with larger cores.⁶ The set-up was kept in dark in a vibration-free atmosphere for about 30 days. The 3-D SLs appear at the air-water interface in the form of a golden yellow film.

The 3-D SLs so fabricated were scooped on carbon coated copper grids and doped silicon substrates, respectively, for high resolution scanning electron microscopy (SEM) and low angle XRD measurements.

Supporting Information (SI) 2

Charge transport measurement methodology: Charge transport measurements were done using a methodology similar to the van der Pauw method. A schematic of the processes involved is shown in **FIG. 3** of the manuscript. The 3-D SLs formed at the air-water interface by the acidification method were carefully scooped on to the surfaces of a quartz or alumina plate (0.2×0.2 cm, thickness=0.1 cm), whose edges were pre-coated with fine quality cello tape strips. Being a Langmuir-type film, the 3-D SLs immediately stick to the surface of the substrates as a robust film. This was then gently dipped in Millipore water (to remove acid impurities if any, as the SLs synthesis was done under acidic conditions) and ethanol successively. The SL layer was allowed to dry under ambient conditions. The film was subjected to vacuum for 3 h. The dried film was examined under a laser microscope to see whether cracks exist on the films. Only robust and crack-free films were used for measurements. Removal of the cello tapes strips leaves the SL layer at the centre of the alumina/quartz plates, which allows its exact measurement of thickness (~1.4 μm) by using a Keyence VK 8500 laser microscope. Ohmic contacts were established with the corners of the SL layer using silver paste (as shown in the schematic in **FIG. 3**). The sample was then mounted on the chamber (a copper cold plate) of a “Janis Research Model CS22-4LF-0-CX Micro-Manipulated Probe Station.” The sample chamber was cooled to 18 K under a vacuum of 10⁻⁴ Pa. Electrical contacts were established with the sample by adjusting the probe tips in desired directions (as shown in **FIG. 3**). A suitable DC current of 1 nA, 10 nA and 100 nA respectively, for SL(I), SL(II) and SL(III) were passed through the Ohmic contacts

labeled A and B and the voltage differences (in the range of ~ 20 mV for SL(I) and ~ 2 mV for SL (III) and a value in between for SL(II) at the base temperature) were measured across the other two contacts C and D. This gives the resistance of the film, $R_{AB,CD}$. In the second step, the same probe currents were passed through the contacts A and D and voltage differences were measured across B and C. This gives the resistance $R_{AD,BC}$. From these, the average resistance R of the films was calculated. The experiments were repeated several times and found to be excellently reproducing.

The I - V characteristics of the samples at base temperature and RT were found to be linear crossing the zero point implying the absence of thermoelectric effects. As a representative case, the I - V characteristic of SL (III) in the base temperature region is shown in **Supporting Information 3**.

Supporting Information (SI) 3

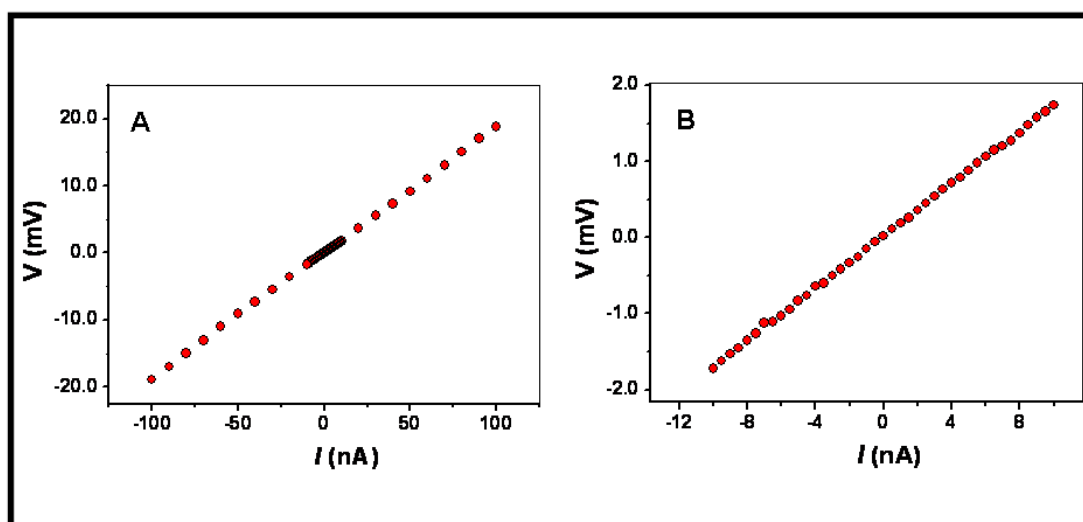
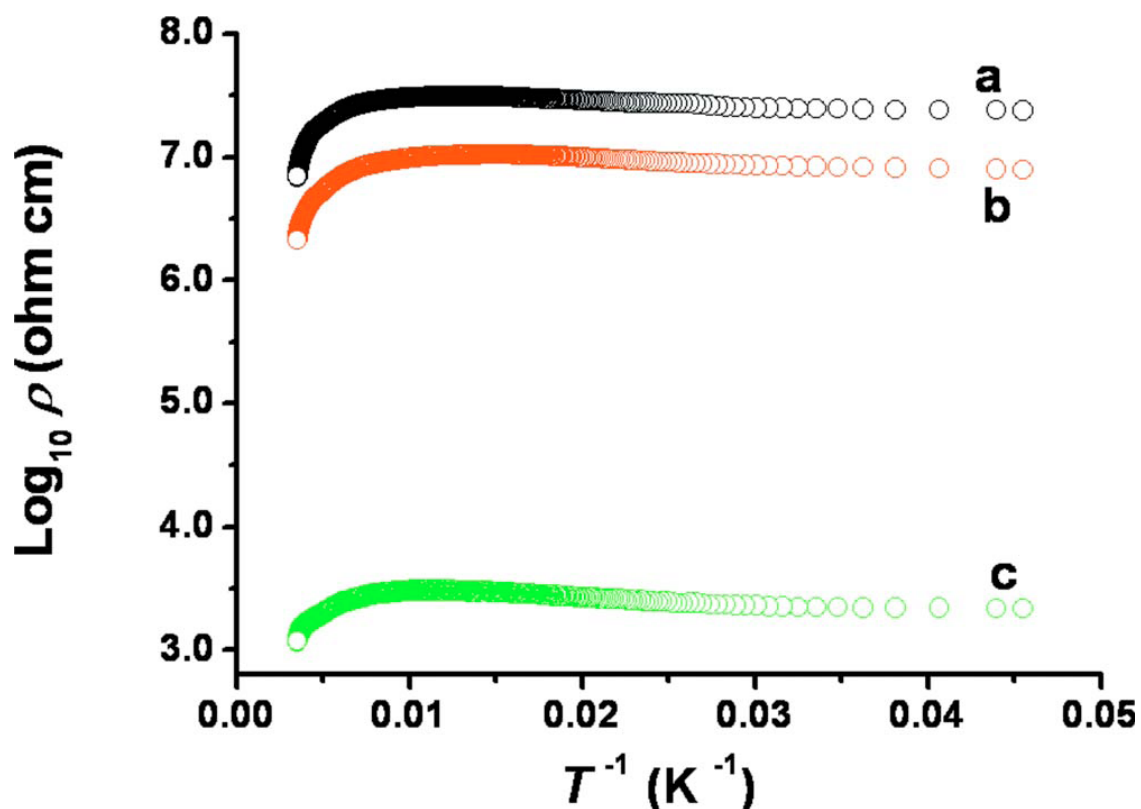


Figure A shows the I - V plot of SL(II) at 20 K (base temperature) showing their linear dependence and crossing of the zero point. **Figure B** shows the expanded version of the same graph near the crossing point.

Supporting Information (SI) 4



Traces a, b and c denote the charge transport behavior of drop-casted Au-MSA MPCs having three different cluster core sizes.⁷ Metallic-like nature was observed at low temperatures and semiconductor nature at high temperatures. There was no transition feature at around 205 K.

References

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