

Control of the Self-Assembly of Alkanethiol-Coated Gold Nanoparticles in the Solid State

By

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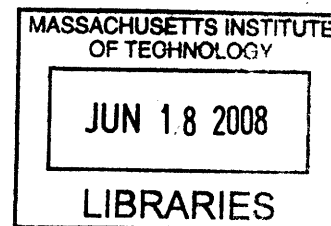
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ABSTRACT

A study of the behavior of nanoparticles in the presence of solvent vapors is presented. Millimeter-scale films of gold nanoparticles, one nanometer thick, are treated with solvent vapors at various temperatures and the behavior of the nanoparticles is tracked over time using transmission electron microscopy. The ultimate goal of this processing is to repair defects such as grains, dislocations, and vacancies in the original superlattice. Additionally, Langmuir-Schaeffer films of gold nanoparticles on water surfaces are subjected to thermal and ultrasonic treatment in an attempt to correct defects in the films, which are then transferred to solid substrates for observation. Unfortunately, none of these approaches is able to reduce the defect concentration in a lattice, although thermal treatment and sonication of Langmuir-Schaeffer nanoparticle films are found to provide a controllable approach to depositing exact double layers of nanoparticles.

CHAPTER 1

Introduction

When cast into the solid state from a colloidal solution, gold nanoparticles begin to exhibit their most interesting and useful characteristics. In a colloidal solution, gold nanoparticles undergo random motion and have a sizeable distance between them, limiting interparticle interactions. When cast into the solid state, nanoparticles can be made to self-assemble such that they are less than one radius apart from one another, bringing them close enough to allow for an optoelectronic interaction.

Each metallic nanoparticle core is coated with an insulating ligand shell, establishing a metal-insulator interface along which surface plasmons can oscillate. As nanoparticles come closer and closer together, the plasmons of each particle can begin to couple and oscillate together. The transmission of surface plasmons between neighboring nanoparticles happens very rapidly, and optoelectronic plasmon waveguides, antennas, and sensors are examples of devices that can theoretically be made using properly arranged nanoparticles¹. The difficulty lies in coercing the nanoparticles into the arrangements necessary to make such devices. The common method of choice is self-assembly, during which the capping ligands on neighboring nanoparticles interdigitate, forming a mesh of molecules. This sort of self-assembly typically yields a hexagonal close-packed arrangement of nanoparticles, as shown in Figure 1a. If controlled correctly, our group has demonstrated 2D monolayers of gold nanoparticles with dimensions on the millimeter scale. However, this self-assembled superlattice is plagued with defects. Just as in an atom-based crystal lattice, gold nanoparticle superlattices exhibit defects such as dislocations, vacancies, interstitials, and grain boundaries, as demonstrated in Figure 1b.

Grain boundaries act to interrupt the transmission of plasmons through a superlattice; dislocations and vacancies act as “hot spots” which dump the energy of plasmons and prevent their transmission. These behaviors may or may not be desirable depending on the intended plasmonic device, but there is currently no way to control the presence of these defects. It is desirable to develop a process which can heal these defects and create a perfect monocrystalline nanoparticle lattice, analogous to the process of annealing an atomic lattice.

The second pillar of my work into the thermal and chemical treatments of nanoparticles will be the assembly of three-dimensional superlattices of alkanethiol-capped gold nanoparticles. In this conformation, the nanoparticles act as the atoms in a 3D atomic lattice, and the alkanethiol ligands are analogous to the bonds that hold atoms together. The nanoparticles are intended to form a sort of meta-material with its own interesting mechanical and optoelectronic properties. For example, a three dimensional lattice with periodically spaced gold nanoparticles has the potential to act as a 3D photonic crystal, permitting certain wavelengths of light and filtering out others.

CHAPTER 2

Background

2.1 Ligand Shell Characteristics

Molecular dynamics simulations have shown that dodecanethiol molecules self-assemble as independent bundles on the surface of a gold nanoparticle², forming an incomplete monolayer with numerous voids around a nanoparticle. The interdigitation of dodecanthiol bundles from neighboring nanoparticles fills these voids and increases the density of ligands around a nanoparticle. As these voids are filled by dodecanethiol from neighboring nanoparticles, the amount of thermodynamically favorable Van der Waals interactions between interdigitated dodecanethiol molecules increases. The close-packing that nanoparticles undergo in the solid state maximizes the amount of interdigitation by bringing nanoparticles as close together as possible.

A three-dimensional lattice of gold nanoparticles is the assembly which leads to the closest packing of gold nanoparticles and hence the greatest amount of Van der Waals interactions. In this arrangement, the metallic nanoparticle cores are analogous to the atoms in an FCC lattice, and the interdigitated dodecanethiol ligands are the bonds that hold atoms together. The process for self-assembling the largest possible 2D and 3D structures requires that nanoparticle ligands be well-extended; in a poor solvent, the solvent molecules will not penetrate into the SAM and instead cause it to “crumple” upon itself because of the repulsion it will feel from the surrounding liquid. This effect is illustrated in Figure 2.

When the ligand shell is well-extended, as in Figure 2a, nanoparticles are able to easily interdigitate their ligands, and neighboring nanoparticles readily assemble into a close-packed arrangement. When their ligand shells are poorly extended in a bad solvent, as in Figure 2b, the

nanoparticle shells will have minimal interdigitation with their neighbors and experience poor self-assembly, more likely forming an amorphous rather than crystalline structure. The value which determines whether a solvent is a good or bad solvent is the solubility parameter, discussed in the next section.

2.2 Solubility Parameters

Every solvent has a solubility parameter which describes the amount of interaction between individual molecules of the solvent. For a species i , the solubility parameter δ_i is defined as:

$$\delta_i = \sqrt{\frac{\Delta E_i^v}{V_i}} \quad (1)$$

Where ΔE_i^v is the energy of vaporization of a species i when it undergoes an isothermal expansion into an ideal gas form at infinite volume; V_i is the molar volume of species i . Simply put, two species with similar solubility parameters will be miscible, and two species with dissimilar solubility parameters will be immiscible. The greater the difference in solubility parameters between two solvents or materials, the less miscible they are. Table 1 gives a list of the organic solvents used in this study and their solubility parameters.

Solvent	Solubility Parameter (MPa ^{1/2})
Hexane	14.9
Dodecane	16.2
Dodecanethiol	17
Carbon Tetrachloride	17.6
Cyclopentane	17.8
Toluene	18.2
Benzene	18.8
Chloroform	19
Dichloromethane	20.2
Dichlorobenzene	20.5
Isopropyl Alcohol	23.5
Ethanol	25.9

Table 1. Solubility parameters of the solvents used in this study. Values taken from [3].

Based on the solubility parameter of dodecanethiol, we are led to believe that the nanoparticles will have an effective solubility parameter of $17 \text{ MPa}^{1/2}$. However, nanoparticles gradually precipitate out of solvents such as dodecane and toluene over a period of days, indicating imperfect miscibility. Laboratory experience has shown that nanoparticles can remain soluble in chloroform solvent for an indefinite period of time, indicating that their effective solubility parameter is closer to that of chloroform, $19 \text{ MPa}^{1/2}$. This disparity in solubility parameter between pure dodecanethiol and dodecanethiol-capped nanoparticles is logical; the dodecanethiol SAM is chemically different from pure dodecanethiol because it is reduced and has no S-H bond. Furthermore, the nanoparticle cores are made of highly polar metal, also acting to increase the effective solubility parameter of the nanoparticles to $19 \text{ MPa}^{1/2}$.

The solubility parameter has implications in determining the best solvent from which to cast nanoparticles, since it will influence how well the ligand shells are dispersed and able to interdigitate. Additionally, the strength of the solvent's Van der Waals interactions with the dodecanethiol molecules will determine how well the nanoparticles mobilize under its influence. This topic is covered in greater detail in Section 2.5.

2.3 Langmuir-Schaeffer Deposition

Langmuir-Schaeffer nanoparticle deposition entails dropping a nanoparticle-containing solution onto a water meniscus. The solvent is chosen to be immiscible with water and spreads as a thin film, one nanoparticle thick, over the meniscus. As the solvent evaporates, the nanoparticle monolayer is left suspended across the surface of the meniscus, and can be transferred to a solid substrate simply by bringing the two into contact.

In our case, the immiscible solution is one of 50:50 by volume dichloromethane:hexane in which nanoparticles are dissolved. Upon coming in contact with the water surface, the

dichloromethane:hexane solution forms a droplet which flows to the edge of the meniscus and begins to evaporate. As the solvent solution flows and evaporates, it leaves behind the nanoparticles dissolved in it as a monolayer at the air-water interface. Double layers and multilayers of nanoparticles form in certain areas on the meniscus, depending on the rate of solvent evaporation and local evaporation conditions in those areas. It is evident to the naked eye which areas are monolayers and which are double or multilayers, and the substrate of interest can be selectively touched only to the areas which have formed a uniform nanoparticle monolayer.

2.4 Pre-casting Treatment of Nanoparticle Monolayers

One aspect of this experiment was to control the grain structure and defect concentration of the nanoparticle monolayer when it is on the water meniscus, prior to being transferred to a solid substrate. We can vary the temperature of the water that provides the meniscus on which the monolayer is formed. This has the effect of accelerating solvent evaporation, which in theory allows less time for nanoparticles to self-assemble out of the solvent solution. Conversely, hotter water increases the temperature of the dodecanethiol SAM's on the nanoparticles, giving them more flexibility. A more flexible SAM on each nanoparticle translates to more mobile nanoparticles, which are able to rearrange themselves and correct defects in the lattice.

Increasing the temperature of the water on which the nanoparticle monolayer forms places two mechanisms in competition. On the one hand, the nanoparticles are more mobile and can both self-assemble more quickly and correct defects post-casting. On the other hand, the solvent in which nanoparticles are suspended evaporates more quickly at the higher temperature, and gives the nanoparticles less time to self-assemble. It should be noted that the water temperature can also be decreased below room temperature to leverage the slower evaporation rate of the solvent and sacrifice nanoparticle mobility.

Another method of improving the Langmuir-Schaeffer monolayer quality is the use of ultrasonic processing. Nanoparticles in solution have a tendency to agglomerate into amorphous 3D masses which can be broken apart using sonication. This indicates that nanoparticles react and are mobilized by sonic waves, an effect that we can employ to repair defects in a 2D Langmuir-Schaeffer monolayer.

2.5 Post-casting Treatment of Nanoparticle Monolayers

Gutierrez-Wing et al⁴ have shown that flowing toluene vapor over disordered gold nanoparticles will mobilize the nanoparticles and encourage them to form initially 2D monolayers and then 3D crystalline superstructures. Extending the idea of solvent vapor mobilization of gold nanoparticles, we can theorize that defects in 2D gold nanoparticle superlattices can be repaired by mobilizing and reflowing the nanoparticles in the lattice to move grain boundaries, annihilate vacancies, and fill voids.

The mechanism for gold nanoparticle mobilization can be thought of as follows. Nanoparticles in a 2D assembly are normally locked into position because their SAM's are densely interdigitated. In order for the nanoparticles to become mobile, the dodecanethiol ligands need to become labile and de-interdigitate. This requires the breaking of Van der Waals bonds between dodecanethiol molecules, which is energetically unfavorable. The presence of a good solvent (solubility parameter $16 - 21 \text{ MPa}^{1/2}$) around the nanoparticles and the dodecanethiol molecules makes the breaking of the dodecanethiol-dodecanethiol interaction less unfavorable. As illustrated in Figure 2, solvent molecules from a good solvent infiltrate the SAM and satisfy the otherwise broken Van der Waals interactions. Under the right conditions, this allows the SAM of one nanoparticle to deinterdigitate from the ones around it and become mobile, with the

ability to migrate grain boundaries, annihilate vacancies and dislocations, and fill voids, the ultimate goal of this study.

CHAPTER 3

Experimental Methods

3.1 Gold Nanoparticle Synthesis

Monodisperse dodecanethiol-capped gold nanoparticles were synthesized using a modified version of the technique reported by Zheng et al⁵. Prior to use, all glassware and stirring bars were soaked in a fresh aqua regia solution, followed by a rinse with distilled water, and then washed with acetone and isopropanol before being blown dry with pressurized air. This level of care was taken to ensure that the glass surface is free of heterogeneous nucleation sites and chemically functionalized surfaces, to which this reaction is particularly sensitive.

A 20 mL solution of Benzene (EMD Chemicals, Inc.), Chloro(triphenylphosphine) Gold(I) (Sigma-Aldrich Co.), and dodecanethiol (Sigma Aldrich Co.) was prepared and stirred at 90 °C for 10 minutes under reflux. A separate solution of 20 mL of benzene and borane tert-butylamine reducing agent (Sigma-Aldrich Co.) was prepared in parallel and stirred at room temperature for 10 minutes. The benzene solution containing borane tert-butylamine was then added all at once to the benzene-gold-alkanethiol solution and heated at 90 °C for one hour. Immediately upon addition of the reducing agent, the reaction mixture began to turn brown, then grey, and eventually a dark purple color. At the end of the hour, the reaction solution was removed from heat and allowed to cool down to room temperature. At this point, 60 mL of ethanol (Pharmco-Aaper) was added to the nanoparticle solution and allowed to sit overnight. After several hours, all of the nanoparticles precipitated out of the ethanol-benzene solution and the supernatant solution was discarded. A mixture of 10:1 by volume ethanol:benzene was prepared, a small volume of which was added to the precipitate and sonicated. Nanoparticles exhibited poor solubility in this solution and precipitated out when centrifuged at 1000 rpm for

five minutes. The supernatant was discarded and the 2 mL centrifuge vials were topped off with 10:1 ethanol:benzene solution. After sonication, this solution was centrifuged again. This sonicate-centrifuge-discard-refill procedure was repeated two more times. With each rinse cycle, the nanoparticles became more soluble in the polar ethanol:benzene solution, presumably because of the removal of unbound dodecanethiol from the self-assembled monolayers (SAM's) on the gold nanoparticles. After the final rinse cycle, the supernatant was discarded and the nanoparticles were dried under vacuum for three hours, producing a highly stable black powder which could be redissolved in a variety of organic solvents.

3.2 Casting Nanoparticle Monolayers Using the Langmuir-Schaeffer Technique

A modified version of the technique developed by Santhanam et al⁶ was used to prepare uniform monolayers of gold nanoparticles, with sizes on the millimeter scale. Powdered nanoparticles, whose synthesis is described in Section 2.1, were dissolved in a solution of 50:50 by volume dichloromethane:hexane with a concentration of 0.5113 mg/mL. A deionized water meniscus was established at the mouth of a glass vial, and a volume between 50-200 μ L of nanoparticle solution was dropped onto the meniscus. The solvent was allowed to evaporate until a monolayer of nanoparticles was clearly visible in the center of the meniscus; a monolayer is differentiated from a double or multilayer by being the lightest shade of pink on the entire meniscus. A double layer of nanoparticles is twice as dark as a monolayer, a difference which is clearly visible to the naked eye.

To transfer the nanoparticle monolayer from the air-water interface, a substrate was lightly touched to the nanoparticle monolayer and pulled away at a 45° angle. The substrates were either amorphous carbon films on copper grids (Ladd Research Co.) or Si₃N₄ film windows on Silicon substrates (Structure Probe Inc.)

3.3 Solvent Vapor Processing of Nanoparticle Monolayers

Large (3 mm x 3mm) gold nanoparticle monolayers were cast onto TEM substrates using the technique described in Section 2.2. The TEM substrates were placed at the bottom of a glass scintillation vial, which was then placed inside a larger glass vial. The space between the inner and outer vials was filled with 2 mL of the solvent of interest, as illustrated in Figure 3. The entire assembly was then either placed in a refrigerator, an oven, or left at room temperature for the duration of the treatment. The TEM substrates were removed from the inner vial periodically to be imaged on a JEOL 200CX transmission electron microscope, and then positioned back to the bottom of the inner vial for further processing.

3.4 Ultrasonic Processing of Nanoparticle Monolayers

An attempt was made to use ultrasonic processing to correct defects in the nanoparticle monolayer formed on a water meniscus using the Langmuir-Schaeffer technique. A nanoparticle monolayer was first formed on a water meniscus using the technique described in the first paragraph of Section 3.2. The vial on which the meniscus and monolayer formed was then placed in the water bath of a sonicator and sonicated for various intervals of time and at different power levels.

3.5 Thermal Processing of Langmuir-Schaeffer Monolayers

Langmuir-Schaeffer monolayers were made using nanoparticles on water meniscuses which varied in temperature. For casting on water at a temperature greater than room temperature, deionized water was heated in an oil bath to the temperature of interest. Care was taken to isolate the water in a closed vial so as to avoid contact or mixing with the oil. Once at the desired temperature, the water was used to create a meniscus away from the oil bath. A Langmuir-Schaeffer film of nanoparticles was then prepared and cast onto a substrate using the

technique described in Section 3.2. For monolayers cast on a meniscus below room temperature, deionized water was cooled to the desired temperature in a refrigerator. A meniscus was then made using this water and a nanoparticle monolayer was established and cast using the technique described in Section 3.2.

CHAPTER 4

Results

4.1 Dodecane Vapor Treatment

Figure 4 shows the effect of room temperature dodecane vapor treatment on gold nanoparticle superlattices cast on amorphous carbon TEM substrates. The lattice is initially well-ordered, with defects such as grain boundaries and vacancies present uniformly throughout the lattice. After 48 hours under dodecane vapor, the nanoparticles are observed forming small islands of stacked nanoparticles, which appear to grow into larger islands after 96 hours under dodecane vapor. Nanoparticle conservation is observed in the formation of voids in the monolayer where nanoparticles were once positioned, but then migrated to form double layers elsewhere. No data is presented for nanoparticles subjected to greater than 96 hours of treatment because the nanoparticle lattice did not undergo additional changes in structure or morphology.

4.2 Isopropyl Alcohol Vapor Treatment

Figure 5 shows the effect of room temperature isopropyl alcohol vapor treatment on gold nanoparticle superlattices cast on amorphous carbon TEM substrates. As with the dodecane treatment, we begin to see double layers forming after two days. However, in the case of dodecane vapor treatment, the double layers are observed forming randomly and evenly throughout the monolayer. In the case of isopropyl alcohol, they form at higher energy locations, namely the interfaces between grain boundaries. After four days, the original monolayer has turned into a multigrained structure with many gaps and randomly dispersed double layer areas. No data is presented for nanoparticles subjected to greater than 96 hours of treatment because the nanoparticle lattice did not undergo additional changes in structure or morphology.

4.3 Toluene Vapor Treatment

Figure 6 shows the effect of room temperature toluene vapor treatment on gold nanoparticle superlattices cast on amorphous carbon TEM substrates. After two days under toluene vapor, the monolayer has developed many gaps, grains, and double-layered regions, possibly in the areas where grain boundaries used to be. After four days under toluene vapor, the voids in the monolayer and the double-layered regions ripened and shrank. No data is presented for nanoparticles subjected to greater than 96 hours of treatment because the nanoparticle lattice did not undergo additional changes in structure or morphology.

4.4 Ethanol Vapor Treatment

Figure 7 shows the effect of room temperature ethanol vapor treatment on gold nanoparticle superlattices cast on amorphous carbon TEM substrates. No appreciable change which is observable using TEM can be seen after four days of ethanol vapor treatment, and the experiment was curtailed after four days because of the lack of change in the structure or morphology of the lattice.

4.5 Chloroform Vapor Treatment

Figure 8 shows the effect of chloroform vapor treatment at 40°C and Figure 9 shows the effect of chloroform vapor treatment at 60°C. The upper limit on the treatment temperature is 61 °C, the boiling point of chloroform. At 40 °C, nanoparticles are seen severely departing from their original positions in the superlattice as soon as one hour after beginning the vapor treatment. Isolated, amorphous aggregates of nanoparticles are seen, along with sporadic voids in the lattice between small grains/islands of nanoparticles. After 20 hours, some well-ordered portions of the lattice remain, but most of the lattice is dissociated into small islands, and no more large aggregates are seen. After nearly a week of chloroform vapor treatment, the lattice is replete with

voids, small island clusters of nanoparticles, and no long range order. An almost identical progression is seen with chloroform vapor treatment at 60 °C, with a loss of order and superlattice integrity occurring even faster due to the elevated temperature.

4.6 Dichloromethane Vapor Treatment

Figure 10 shows the effect of dichloromethane vapor treatment at room temperature (22-25 °C) and 40 °C. The upper limit on the treatment temperature is 39.8 °C, the boiling point of dichloromethane. Dichloromethane was chosen as a solvent because it is structurally identical to chloroform except for the presence of a hydrogen atom in dichloromethane in place of a chlorine atom in chloroform. This makes it a less active solvent than chloroform, and the hope is that dichloromethane will be less likely to disrupt the nanoparticle superlattice.

The progression from an ordered superlattice to a disordered one happens more slowly with dichloromethane than with chloroform, but the resulting lattice is still the same as the one achieved under chloroform vapor. It is also observed that the loss of order occurs more rapidly with room temperature dichloromethane, which is to be expected.

4.7 Sonication of Langmuir-Schaeffer Films

Nanoparticle monolayers formed at the air-water interface of a water meniscus (using the Langmuir-Schaeffer technique discussed in Section 2.3) were treated with ultrasonic sound waves and then cast onto TEM substrates. Figure 11 shows the effect of sonication processing of various durations and power levels on the self-assembly of nanoparticle monolayers. Sonication at 30 Watts for 30 seconds and sonication at 60 Watts for 30 seconds resulted in no noticeable changes in the monolayer. However, sonication of the Langmuir-Schaeffer monolayer at 90 Watts for 60 seconds yielded a superlattice with large (micron scale), exact double layers of nanoparticles. Figure 12 illustrates the two types of packing seen in the rightmost image of

Figure 11; the grid-like pattern in Figure 11 is the close-packed stacking scheme in Figure 12. The rings seen in Figure 11 are nanoparticle double layers exhibiting ring-like packing, shown in Figure 12.

4.8 Thermal Treatment of Langmuir-Schaeffer Films

Nanoparticle monolayers were formed at the air-water interface of a water meniscus using the Langmuir-Schaeffer technique described in Section 2.3. The temperature of the water onto which the monolayers were cast varied from 4 °C to 95 °C; Figure 13 shows the effect of this variation.

When Langmuir-Schaeffer films were cast on water surfaces with temperatures below 50 °C, no new effects were observed. When the water was at 50 °C, the nanoparticle monolayers began to overlap and form double layers at their grain boundaries. At 75 °C, some double layer formation is observed, but most areas are still multi-grained monolayers. At 95 °C, double layers of nanoparticles are observed almost everywhere, with isolated islands of multilayers in a few regions of the film.

CHAPTER 5

Discussion

The vapors of “good” solvents tested in this study, those with solubility parameters close to that of dodecanethiol, were found to disrupt and introduce many defects into the initially well-ordered nanoparticle superlattice. The theory I present for this behavior is as follows: with no solvent vapor present, it is highly unfavorable and energetically expensive to deinterdigitate the SAM’s of two nanoparticles. Many Van der Waals interactions have to be disrupted, and a substantial amount of energy must be input to accomplish this, as shown by the red curve in Figure 14. When the vapor of a good solvent is present, the vaporized solvent molecules are able to move into the positions where Van der Waals interactions were broken in the dodecanethiol and develop new Van der Waals interactions. As shown by the blue curve in Figure 14, the net increase in energy for this process is much smaller than that for when the SAM’s de-interdigitate with no solvent present, because of the small amount of net unsatisfied Van der Waals forces.

The presence of a solvent makes it energetically possible for two SAMs to de-interdigitate; when the solvent vapor is removed from the system, the nanoparticles are “quenched,” or frozen in the position they were in when solvent vapor was present. It is this quenching which ruins the initially well-ordered superlattice because it does not give the nanoparticles time to reassemble into a well-ordered long-range hexagonal arrangement.

Sonication has been seen to break apart self-assembled nanoparticles when they are in the liquid phase, and we see that it mobilizes them when in a Langmuir-Schaeffer film. The ultrasonic pressure waves are able to input enough mechanical energy to physically de-interdigitate the SAMs of neighboring nanoparticles. It is unclear by which process the nanoparticles rearrange into a double layer, though it may simply be a re-interdigitation process.

Depositing Langmuir-Schaeffer films onto heated or cooled water menisci puts two effects into competition: with increasing water temperature, the solvent evaporates faster and the nanoparticles are given less time to self-assemble before the solvent is removed and they are frozen in place. However, the nanoparticles are also more mobile at higher temperatures, allowing them to form higher-quality lattices and multiple layers. Which of these effects is dominant can't be determined from our data, since we see the formation of double layers at higher temperatures, and these double layers can form either as a result of greater nanoparticle mobility or a reduced deposition time.

CHAPTER 6

Conclusions

As shown in Figures 5 – 13, a technique was not found to effectively correct defects in nanoparticle superlattices. Every solvent except ethanol was found to disrupt the lattice by forming voids, small grains, multilayers, and disordered aggregates. A theory was developed which posits that the solvent vapor is able to mobilize nanoparticles by allowing them to deinterdigitate their self-assembled monolayer (SAM) shells from the SAMs of neighboring nanoparticles. When the solvent vapor is present, the nanoparticles are mobile and behave as a collective liquid; once the solvent vapor is removed, the nanoparticles are quenched, fail to organize into an ordered arrangement, and form a highly defective lattice. This may or may not be a desirable effect, depending on the final device and the preferred nanoparticle arrangement. However, two techniques were developed which controllably deposit exact double layers of gold nanoparticles by either sonicating a Langmuir-Schaeffer nanoparticle film or depositing it on a heated water meniscus.

Future Work

Based on the work presented here, I can make recommendations for future work which could be done in an attempt to find a method for correcting defects in nanoparticle superlattices. First, a greater variety of solvent vapors ought to be tested, running the entire spectrum of solubility parameters, each at a variety of temperatures, from below 0 °C up to the boiling points of the solvents. This work could be coupled with environmental transmission electron microscopy (ETEM), which allows for real-time in-situ observation of the nanoparticles as they

undergo vapor treatment. ETEM observation would clearly elucidate the mechanism by which the nanoparticle superlattices are disrupted by the solvent vapors.

The solvent quenching theory presented earlier claims that the nanoparticles are frozen in place from their mobile positions when a solvent vapor is removed from their environment. If this is the cause of poor superlattice quality, the solvent vapor ought to be slowly and controllably removed from the nanoparticle environment, so that nanoparticles are slowly and gently driven to reassemble into structures with long-range order.

Additionally, work in our group has been done on casting nanoparticles into linear nanoscale patterns, mostly channels 50-100 nanometers wide. The presence of confining walls and barriers limits the mobility of the nanoparticles and prevents them from ripening into small grains and islands. If the nanoparticles are spatially constrained, it may be possible to induce the correction of defects in these confined regions and achieve perfect nanoparticle assemblies.

Finally, substrate pretreatment is a potential avenue for controlling the behavior of nanoparticles in the solid state. The adherence of the nanoparticles to the substrate depends on its hydrophobicity or hydrophilicity. If there is good adhesion between the nanoparticles and the substrate, then they will be less mobile and less likely to form multilayers during solvent vapor treatment. The opposite is true if there is poor adhesion between the nanoparticles and substrate. The substrate-nanoparticle interaction can be leveraged to control how nanoparticles assemble on the substrate and react to subsequent vapor treatments.

CHAPTER 7

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FIGURES

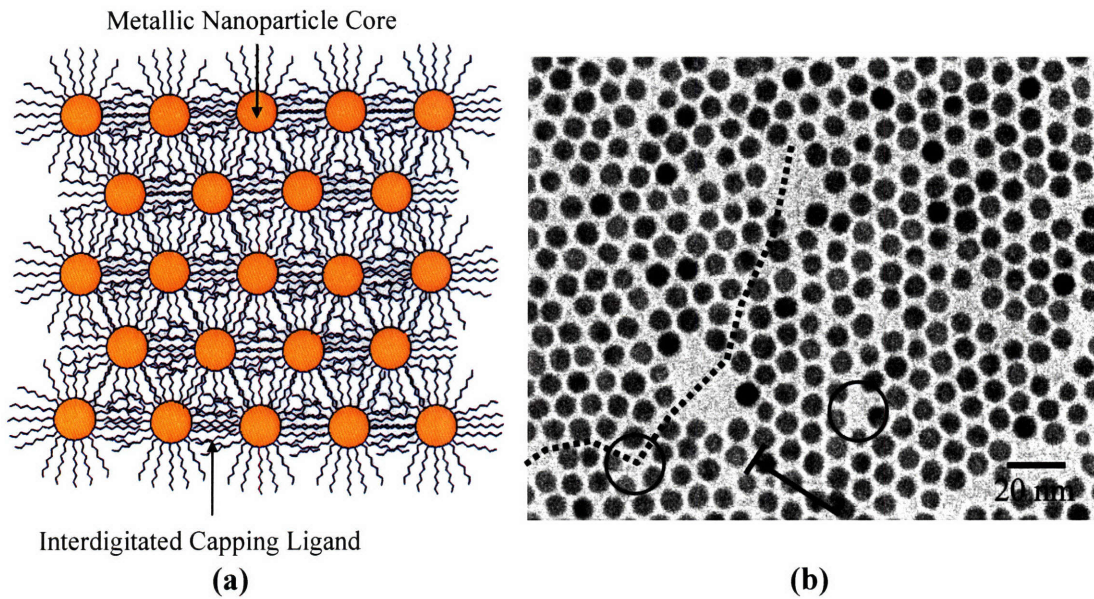


Figure 1. (a) A schematic of how gold nanoparticles self-assemble through the interdigitation of their ligand shells. (b) A TEM image of self-assembled gold nanoparticles capped with dodecanethiol. A grain boundary between grains of different orientation is shown by the dotted line. Examples of single nanoparticle vacancies are circled; large voids are obvious in the image. A dislocation line defect is indicated at the bottom of the image.

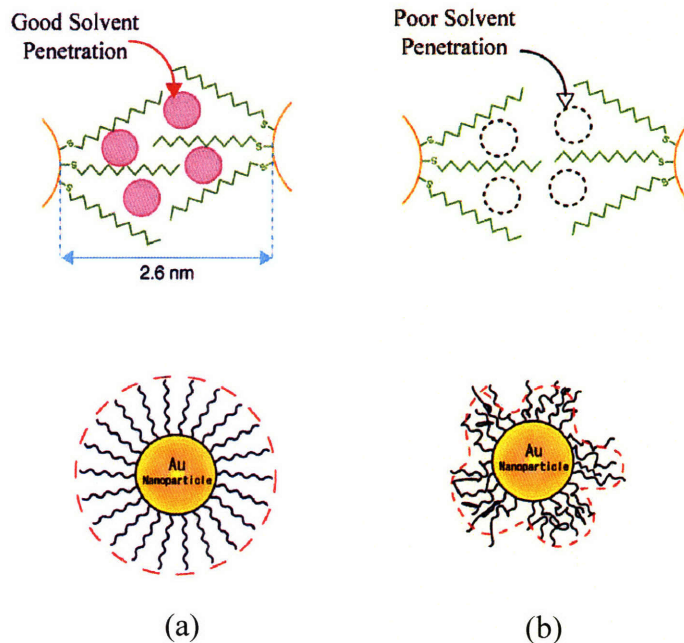


Figure 2. Comparison of the structure of the SAM on a gold nanoparticle in (a) a good solvent and (b) a bad solvent. Image courtesy of [7].

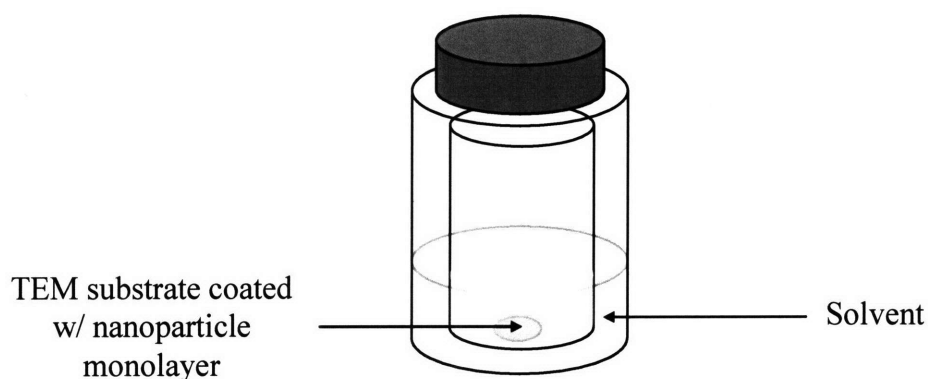


Figure 3. An illustration of the setup used to perform solvent vapor treatments on gold nanoparticle monolayers. A small open-top glass vial is placed inside a larger glass vial. A TEM substrate is placed at the bottom of the smaller vial, and the space between the vials is filled with the solvent whose vapor will interact with the nanoparticle superlattice. The larger vial is then capped to seal in the solvent vapor.

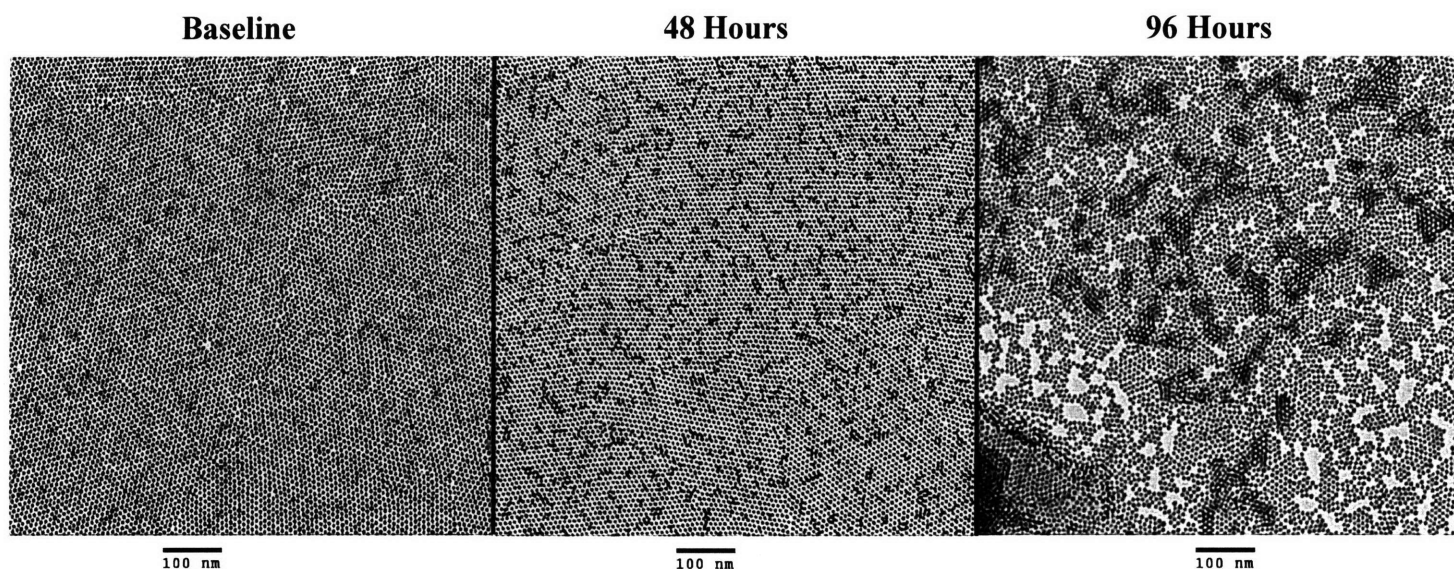


Figure 4. TEM images demonstrating the effect of room temperature dodecane vapor treatment on gold nanoparticle superlattices. The leftmost image is the baseline monolayer which has not been subjected to vapor processing. The middle image is the nanoparticle superlattice after 48 hours under dodecane vapor, and the rightmost image is the superlattice after 96 hours under dodecane vapor.

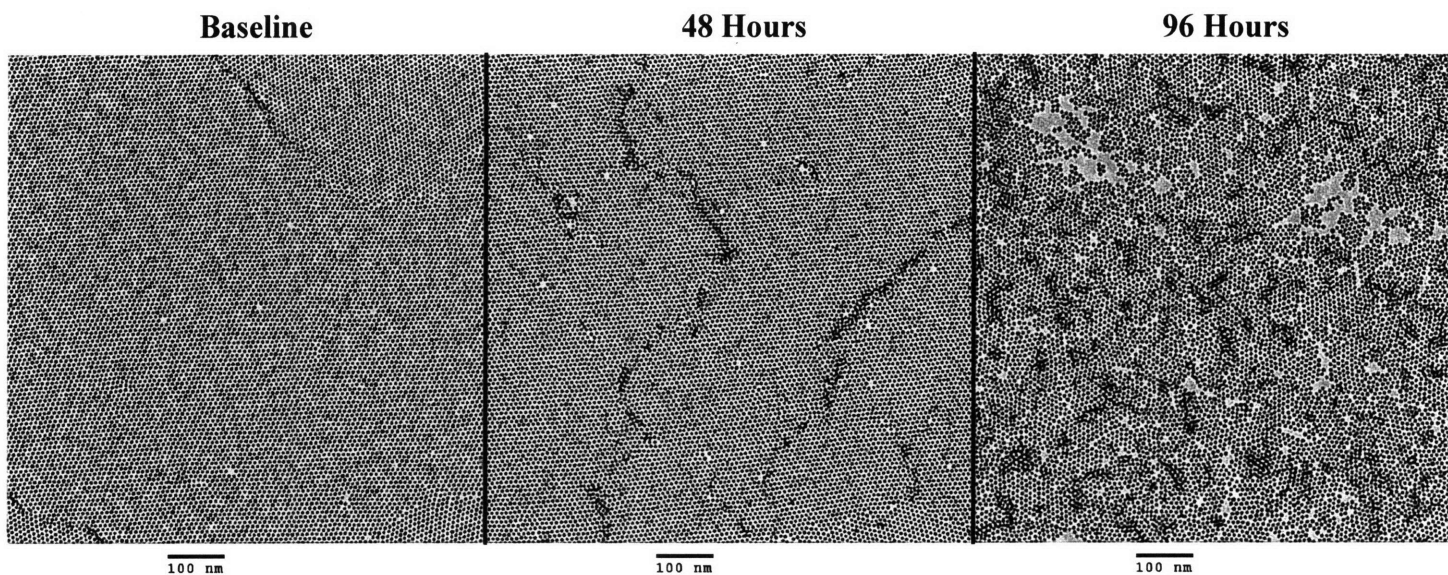


Figure 5. TEM images demonstrating the effect of room temperature isopropyl alcohol vapor treatment on gold nanoparticle superlattices. The leftmost image is the baseline monolayer which has not been subjected to vapor processing. The middle image is the nanoparticle superlattice after 48 hours under isopropyl alcohol vapor, and the rightmost image is the superlattice after 96 hours under isopropyl alcohol vapor.

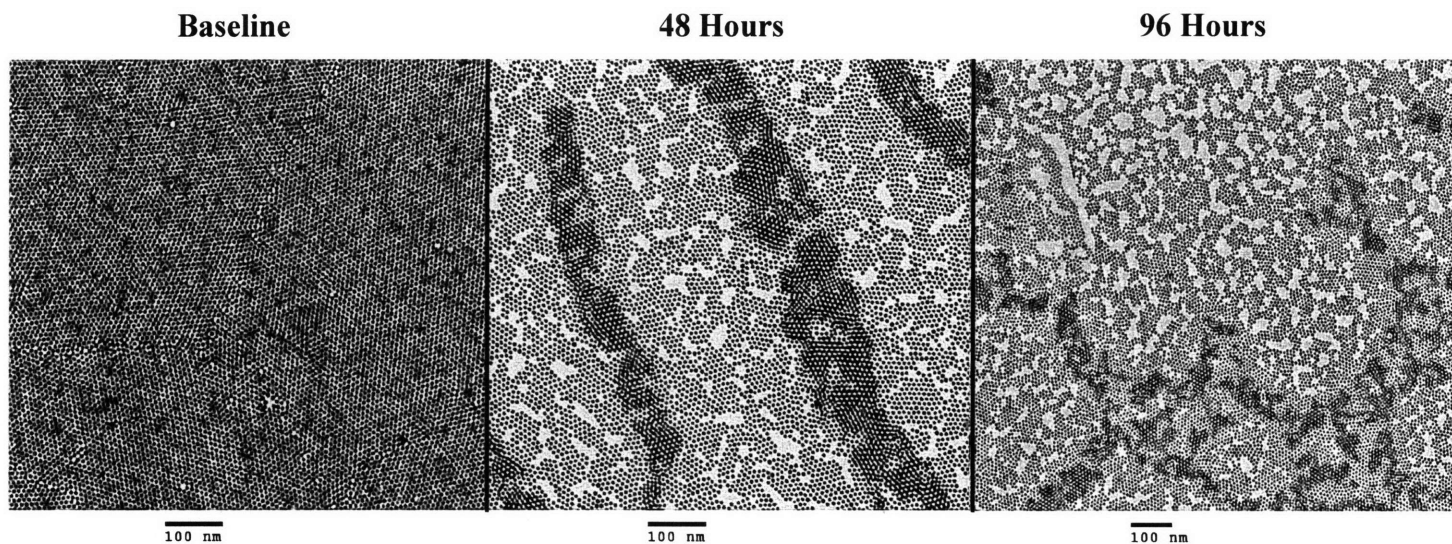


Figure 6. TEM images demonstrating the effect of room temperature toluene vapor treatment on gold nanoparticle superlattices. The leftmost image is the baseline monolayer which has not been subjected to vapor processing. The middle image is the nanoparticle superlattice after 48 hours under toluene vapor, and the rightmost image is the superlattice after 96 hours under toluene vapor.

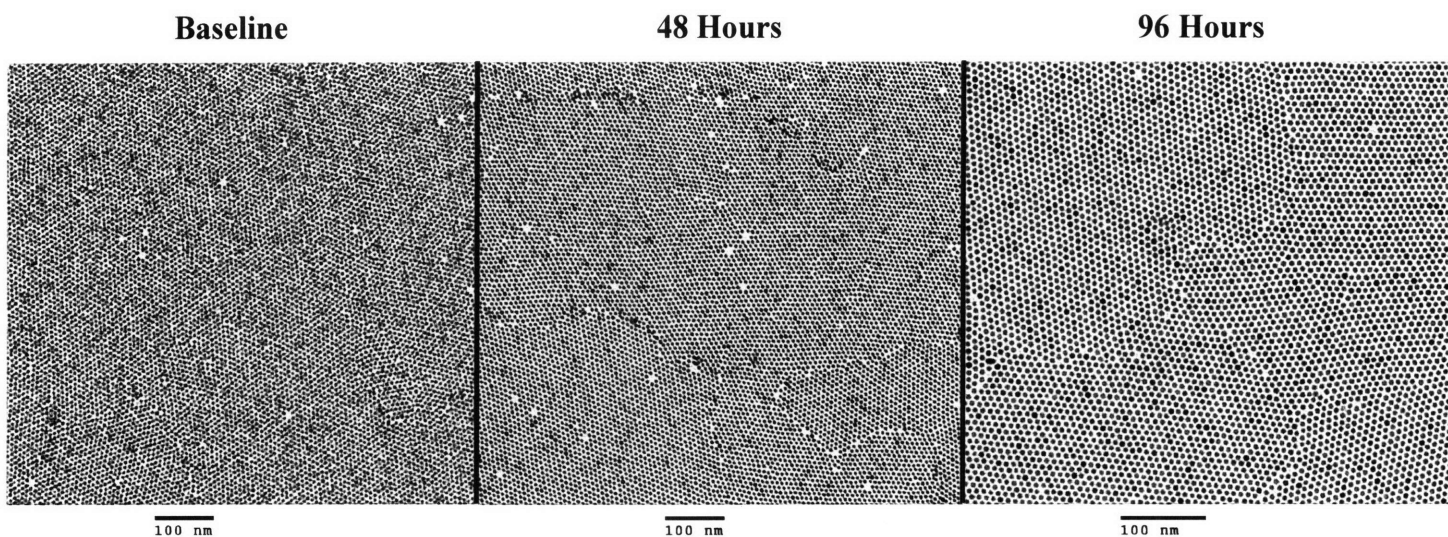


Figure 7. TEM images demonstrating the effect of room temperature ethanol vapor treatment on gold nanoparticle superlattices. The leftmost image is the baseline monolayer which has not been subjected to vapor processing. The middle image is the nanoparticle superlattice after 48 hours under ethanol vapor, and the rightmost image is the superlattice after 96 hours under ethanol vapor.

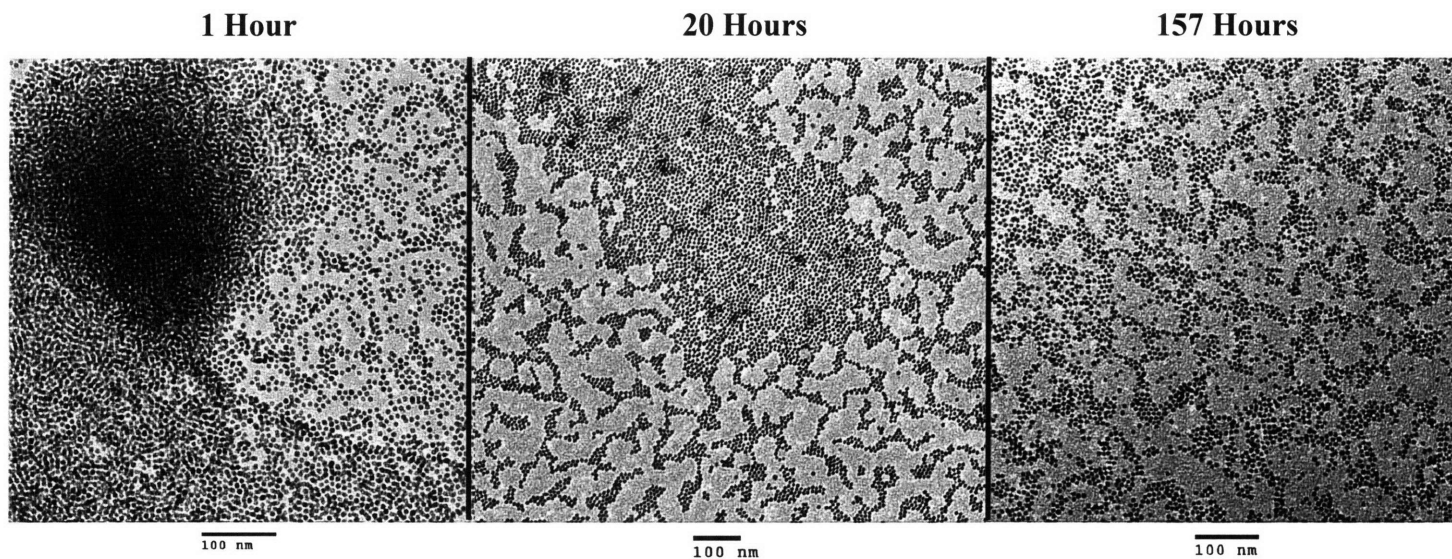


Figure 8. TEM images demonstrating the effect of chloroform vapor treatment on gold nanoparticle superlattices at 40 °C. The leftmost image is a monolayer which has been subjected to vapor processing for one hour. The middle image is the nanoparticle superlattice after 20 hours under chloroform vapor, and the rightmost image is the superlattice after 96 hours under chloroform vapor.

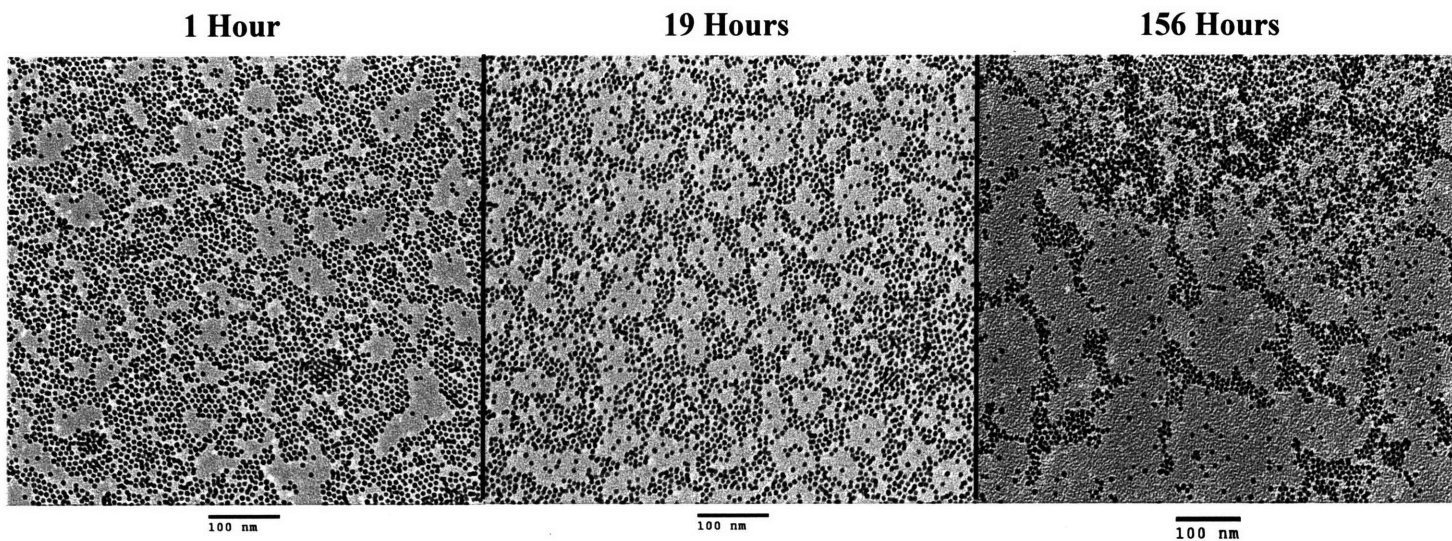


Figure 9. TEM images demonstrating the effect of chloroform vapor treatment on gold nanoparticle superlattices at 60 °C. The leftmost image is a monolayer which has been subjected to vapor processing for one hour. The middle image is the nanoparticle superlattice after 19 hours under chloroform vapor, and the rightmost image is the superlattice after 156 hours under chloroform vapor.

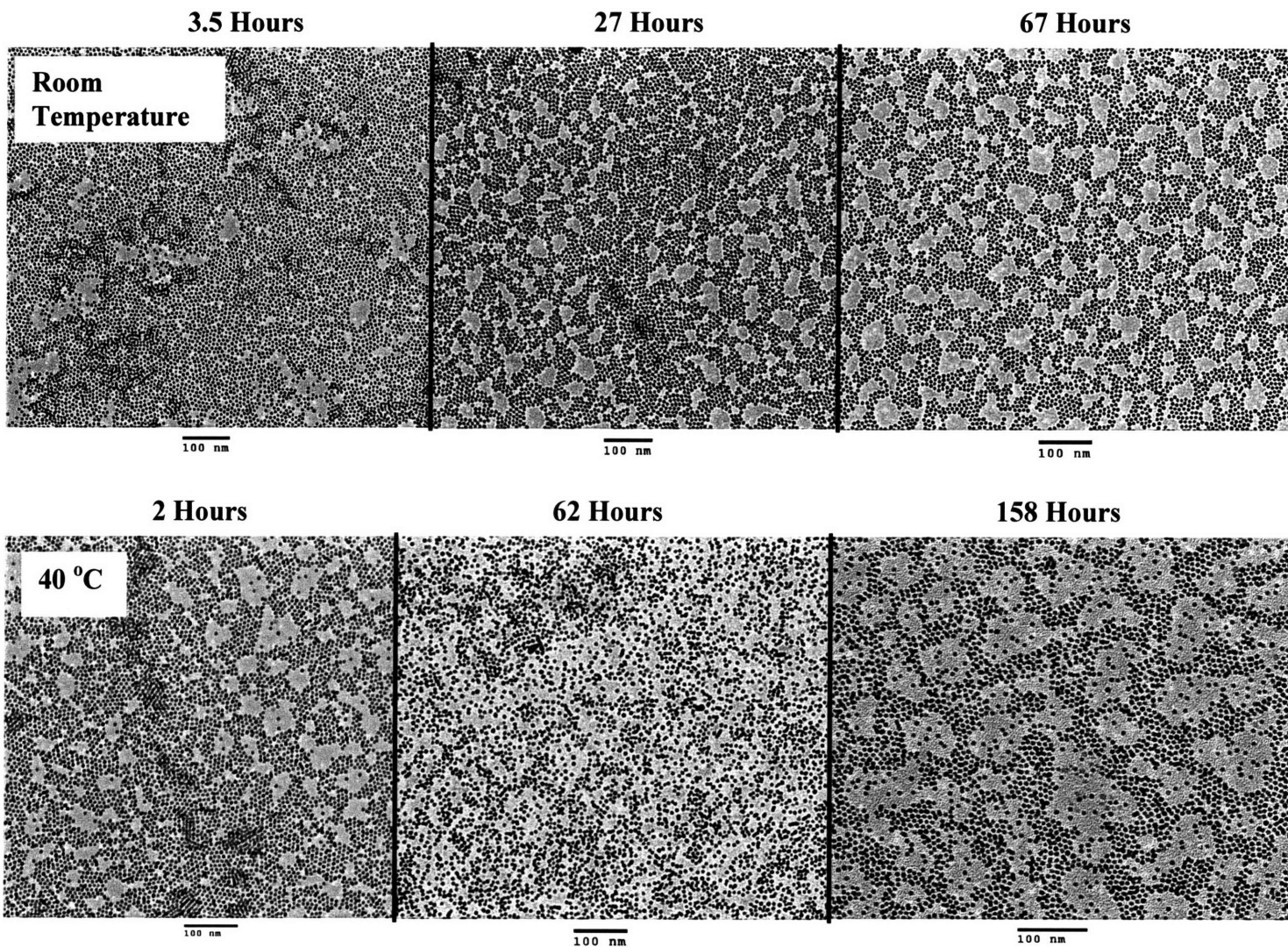


Figure 10. TEM images demonstrating the effect of dichloromethane vapor treatment on gold nanoparticle superlattices at room temperature and 60 °C. The upper row of images is the behavior of an initially well-organized nanoparticle superlattice under room-temperature dichloromethane vapor for the indicated number of hours. The lower row of images is a different superlattice treated with dichloromethane vapor at 40 °C

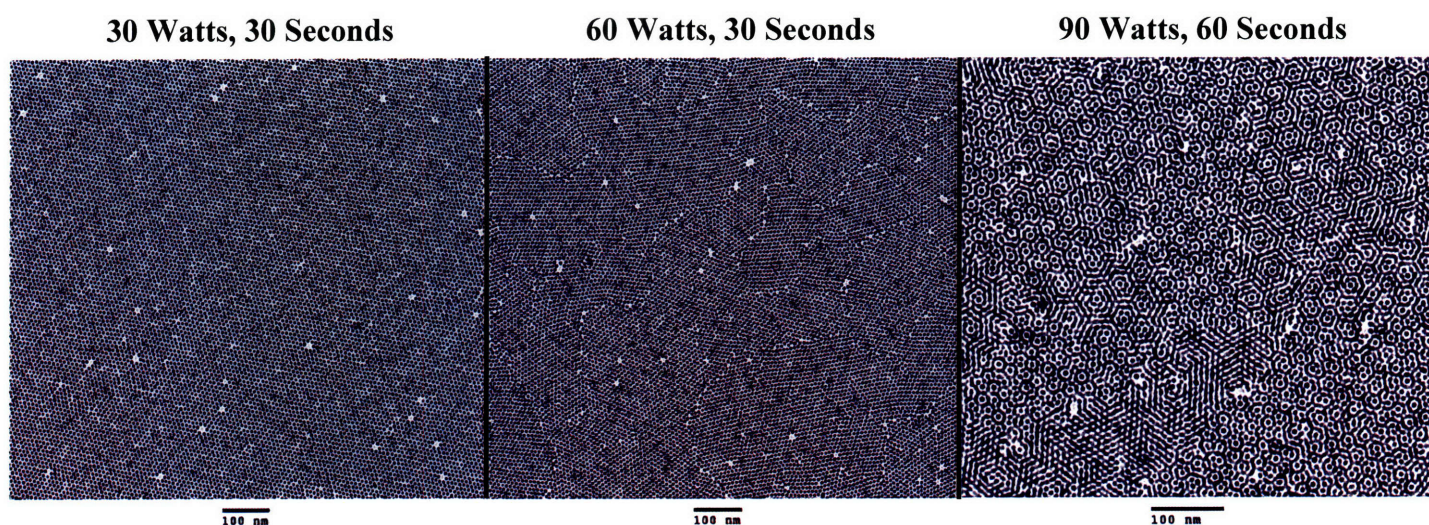


Figure 11. Effect of ultrasonic treatment on Langmuir-Schaeffer films of gold nanoparticles. The indicated values are the power level at which the nanoparticles were sonicated and the duration.

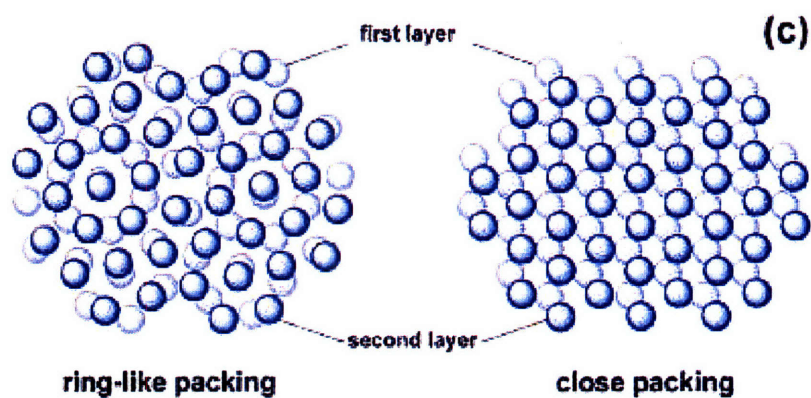


Figure 12. Two types of packing which double layers of nanoparticles can undergo. The rightmost scheme is the most energetically favorable, though both are observed in practice.

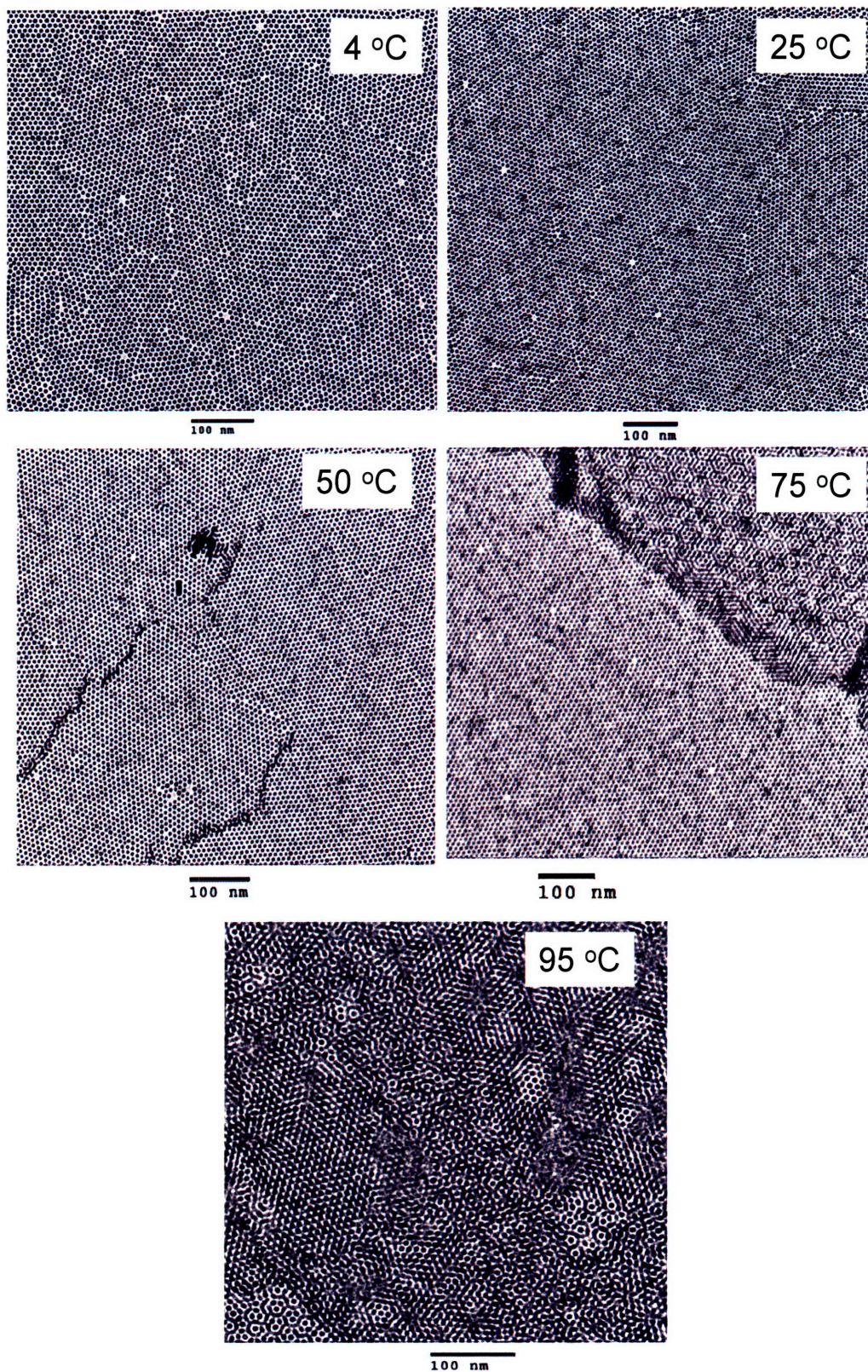


Figure 13. TEM images of gold nanoparticle Langmuir-Schaeffer films deposited on heated or cooled water meniscuses of temperature indicated in the upper right of each image.

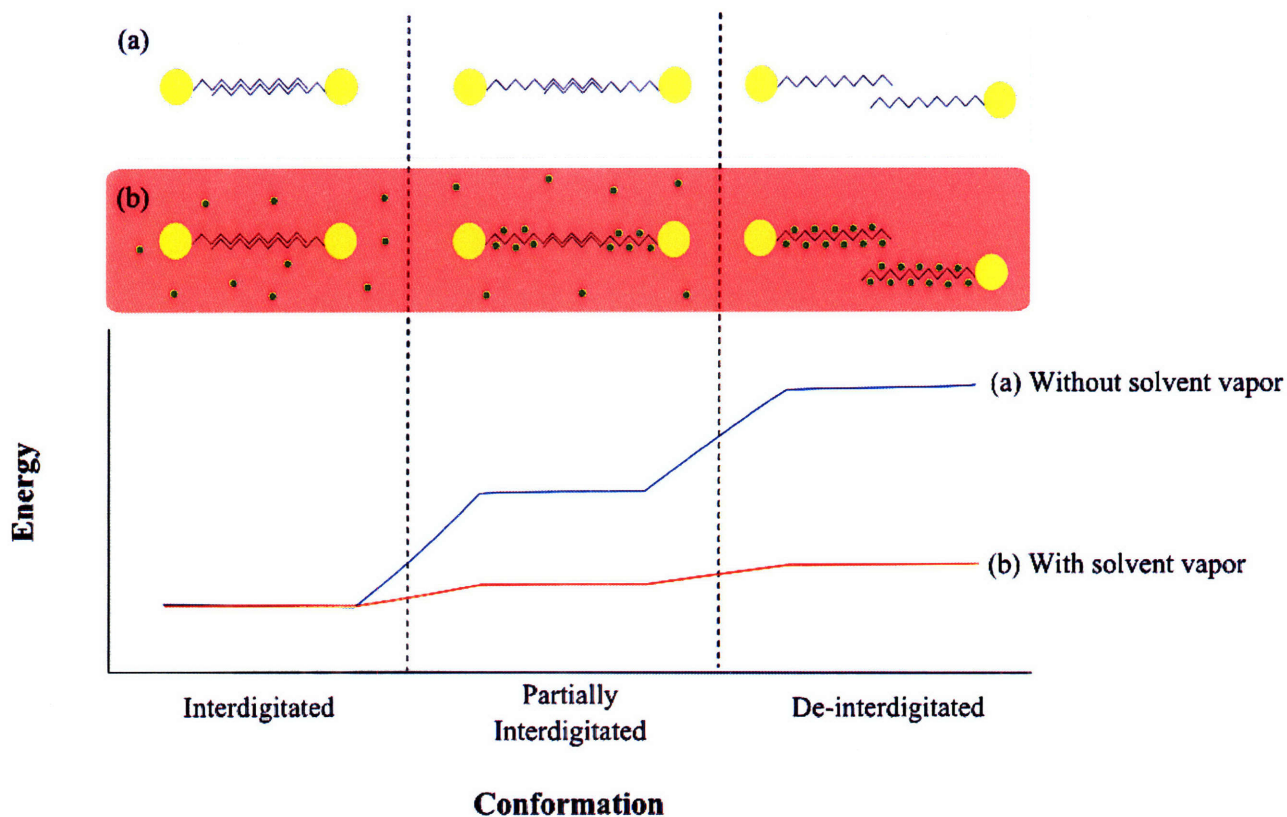


Figure 14. A diagram illustrating the energetics of de-interdigitation of dodecanethiol-capped gold nanoparticles. In pathway (a), the nanoparticles begin with interdigitated ligands which then begin to break Van der Waals interactions in their ligand shells as they are pulled apart. The energy necessary to do so is plotted on the graph as a blue line. In pathway (b), the vapor of a good solvent is present. The vapor molecules (green) move in and satisfy the broken Van der Waals interactions, thus making the de-interdigitation more favorable and less energetically demanding, as shown by the red line in the plot. The presence of a solvent vapor makes it easier for nanoparticles to de-interdigitate their SAMs and depart from their initial equilibrium lattice positions; when the solvent vapor is rapidly removed, they are quenched and do not reassemble into a hexagonal lattice.