Nanoscale Faceting and Ligand Shell Structure Dominate the Self-Assembly of Nonpolar Nanoparticles into Superlattices

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1. Introduction

Nanoscale self-assembly at liquid–solid interfaces is a route for nanostructure engineering with broad scientific and technological applications and occurs in a broad range of natural phenomena. Control of superlattices from nanoparticles (NPs) is achieved by changing variables such as surface ligands, particle shape, size distribution, solvent, and solvent evaporation rate. Self-assembly at the solid–liquid interface can be driven by electrostatic and van der Waals (vdW) interactions between particles and substrate, often enhanced by the confinement of evaporating liquids. Targeted modification of substrates at different length scales enables the templated self-assembly of particles, a crucial step in the creation of functional electronic devices and sensors. The effect of the substrate’s structure at molecular length scales and its interactions with the particles on the resulting assembly dynamics and morphologies are not fully understood.

Ex situ studies cannot distinguish NP self-assembly in bulk liquid from the effects of capillarity. They also do not provide insight into the dynamics of self-assembly processes, while microscopy and diffraction methods are limited in the provided nanoscale information occurring directly at the surface in liquid and prior to drying. This deficiency in experimental methods limits the current understanding of nanoparticle self-assembly for nonpolar dispersions, where short-range interactions can outweigh electrostatic forces. In situ observation of particle self-assembly provides a scale-bridging picture that gives insight into molecular interactions and their role in nanoscale structure formation. Nanometer resolution has been achieved at the solid–liquid interface using liquid-phase electron microscopy for investigations of, for example, self-assembly, Brownian motion, dynamic structural analysis, material growth, electrochemical reactions, as well as topics in the life sciences.

In this work, liquid-phase scanning transmission electron microscopy (LP-STEM) was used to study the assembly of NP superlattices at the interface of a nonpolar solvent and silicon nitride (SiN) surfaces that were grafted with alkyl silanes having...
different chain lengths. Colloids of oleylamine-capped gold NPs (AuNPs) in two organic solvents (cyclohexane and toluene) that differ in their dipole moment were brought on the substrates, and particle assembly was observed. We studied to what extent the strength of the substrate–AuNP interactions determined the onset of self-assembly and the resulting geometric patterns of the assembled structures. Different geometric patterns were observed, depending on the substrate’s polarity and solvent. Interpretation of experimental results was supported by comparison with Langevin dynamics simulations of AuNP self-assembly during Brownian motion to examine the role of substrate–NP interactions balanced with the influence of the NP’s core shape and dipole. The in situ investigation of AuNP self-assembly in liquid revealed that the assembled superlattices can be completely changed by increasing the thickness of the alkyl monolayer coated on the substrate surface. The latter “minor” modification of the substrate–liquid interface radically changed the symmetry of the self-assembled superlattice.

2. Results and Discussion

2.1. LP-STEM of Self-Assembled AuNP Superlattices

3D AuNP superlattices self-assembled at the solid–liquid interface were investigated under different conditions with varied substrate surface functionalization and (nonpolar) solvents. AuNPs with a core diameter of $8.2 \pm 0.1$ nm (standard deviation) and an oleylamine shell were dispersed\cite{3a} in cyclohexane or toluene with dipole moments of 0.0 and 0.31 Debye (D), respectively. The particles formed stable dispersions without agglomerates in both solvents (Figure S1, Supporting Information). Self-assembly took place on a SiN membrane mounted on a silicon microchip (Figure 1). Each microchip underwent an oxygen plasma treatment to create polar hydroxyl groups on its SiN surface and was then used “as is” or coated with a self-assembled monolayer (SAM). We used trichloro(hexyl)silane (6C), trichloro(octadecyl)silane (18C), and trichloro(triacontyl) silane (30C) to obtain SAMs with different thicknesses (Figure 1a). The plasma-treated SiN is referred to as SiN-P in the following, while alkyl-silane-modified surfaces are referred to as SiN-6C, SiN-18C, and SiN-30C. The contact angle of water on the SiN microchips increased from 25° to 108° for SAMs with increasing molecular lengths (Figure S2, Supporting Information). The resulting coatings on the modified SiN surfaces appeared uniform in electron and optical microscopy (Figure S3, Supporting Information) after washing, but molecular densities may have varied between uniform SAM islands.\cite{18}

The self-assembled AuNP superlattices were imaged by LP-STEM.\cite{3b} A microchip was first placed in the slot for two stacked microchips in the tip of a liquid flow specimen holder. AuNP dispersions in cyclohexane or toluene were drop-cast onto the microchip (Figure 1b). The AuNP-dispersion droplet was then enclosed by placing a second microchip upside down on the droplet. A spacer at the corners of the second microchip set the liquid thickness to a minimum of 150 nm (Figure 1c). Finally, the microchip slot in the tip of the liquid flow holder
was closed by placing a lid, thus forming a liquid cell suitable for the vacuum environment of the electron microscope (Figure 1d). Using LP-STEM in dark field mode benefits the detection of Au due to the high atomic number (Z) contrast in the low-Z liquid layer. [19] LP-STEM is particularly suitable to study high-Z-containing soft matter in liquid. [17a] Soft matter here refers to the self-assembled superlattices that undergo dynamic changes at an energy scale comparable with thermal energy (kT).

2.2. AuNP Self-Assembly on Different Substrates

We observed significant attraction of the AuNPs toward the SiN-P surface in both solvents (Figure S4, Supporting Information), resulting in the formation of a single or double layer of AuNPs, as was visible from two distinct gray levels above the background level (Figure 2a and Figure S5a, Supporting Information). Here, dark-field LP-STEM resulted in a brighter area where the material was denser than its surroundings. Images

Figure 2. LP-STEM images of AuNP self-assembled patterns in cyclohexane. a) AuNPs assembled on a plasma-cleaned SiN surface (SiN-P). Electron dose \( D = 173 \text{ e}^{-/\text{Å}^2} \). Liquid thickness \( h = 0.4 \mu\text{m} \). The fast Fourier transform (FFT) in the inset reveals a hexagonal symmetry of the indicated area. b) 3D model construction of AuNP assemblies on a plasma-treated SiN-P surface forming a hexagonal close-packed (hcp) structure. c) AuNPs assembled on a SiN surface coated with trichloro(hexyl)silane (SiN-6C) formed regions with simple hexagonal (sh) symmetry (consisting of perfectly overlapping AuNPs visible as bright spots) coexisting with undefined structures formed by partially overlapping AuNPs, see “sh” and “dqc” markers. \( D = 16 \text{ e}^{-/\text{Å}^2}, h = 2.4 \mu\text{m} \). The inset shows the FFT of the indicated area. d) Magnification of the simple hexagonal (sh) lattice and dodecahedral quasi-crystal (dqc) rings formed on SiN-6C. The models below illustrate the 3D arrangement of AuNPs in the highlighted sh and dqc structures. e) LP-STEM images of AuNPs deposited on trichloro(octadecyl)silane-coated SiN-surfaces (SiN-18C) with body-centered cubic (bcc) assembly; the inset shows the FFT pattern of the indicated area with \( D = 23 \text{ e}^{-/\text{Å}^2}, h = 1.6 \mu\text{m} \). f) Assembly model illustration bcc AuNP structures on trichloro(octadecyl)silane-modified (SiN-18C) substrate. LP-STEM images with examples of AuNP positions highlighted with transparent circles of different colors based on the 3D geometry reflected in the schematics. The first layer of AuNPs is colored light yellow, and the second layer of AuNPs is colored dark yellow. The measured AuNP center-to-center (C-C) distances in vertical projection are indicated.
at higher magnification revealed a self-assembled pattern with uniform hexagonal symmetry (Figure 2b) similar to previously found superstructures of such particles.\textsuperscript{[3a]} The bright oval patterns at the locations of the individual NPs suggest partly overlapping particles from the first and the second layer, with two discrete signal levels (Figure S5b, Supporting Information), indicating hexagonal close-packed (hcp) symmetry. The fast Fourier transform (FFT) of the squared area of Figure 2a reveals the presence of a hexagonal layout of the AuNP double layer on the SiN-P surface. The hexagonal first layer of AuNPs (circled in red) appears continuous despite the presence of the second layer assembled on top, suggesting that the second layer (circled in blue) formed after the first layer. Analysis of the superlattice-covered areas in 30 recorded images of the SiN-P sample showed that the superlattice structure was 99.8% hcp (Table S1, Supporting Information).

Different packings were observed for the double layers formed on the SiN-6C surface (Figure 2c,d and Figure S5, Supporting Information): vertically overlapping AuNPs formed regions of simple hexagonal (sh) symmetry; lines were observed to be composed of partially overlapping AuNPs (marked by “-” in Figure 2c), while elsewhere central particles were surrounded by circles of partially overlapping AuNPs, forming dodecahedral quasi-crystal (dqc) rings (Figure 2d and Figure S5c, Supporting Information).\textsuperscript{[20]} A quasi-crystal is defined as a crystal that lacks periodicity but still exhibits diffraction peaks/spots.\textsuperscript{[21]} Quasi-crystals can show rotational symmetries that are incompatible with periodicity, but this is not always the case.\textsuperscript{[20]} A characteristic feature of the pattern is the presence of bright spots of two fully overlapping AuNPs surrounded by a curved chain of partially overlapping AuNPs. Similar patterns were observed previously for SiN-P in toluene.\textsuperscript{[13]} Some other areas of the SiN-6C samples contained superlattices of hcp symmetry. The fractions of the different structures are summarized in Table S1 (Supporting Information). We do not know at present whether the observed heterogeneities in the assembled superstructures are connected to differences in the local molecular nature of the substrate. It is conceivable that superstructures that are defined by deep minima in their energy landscape are less sensitive to such variations, which could explain the differences in homogeneity that we observe for different cases. It is also possible that the contribution of particle-substrate interactions is stronger for some superlattices or that different organic coatings exhibit different degrees of variability.

On the SiN-18C surface, we observed mostly patterns of body-centered cubic (bcc) symmetry (Figure 2c), a similar structure observed in our previous findings of SiN-P in hexadecane.\textsuperscript{[3a]} Smaller patches were arranged in hcp and dqc (see Table S1, Supporting Information, for areal fractions). We observed two different types of cubic AuNP arrangements (Figure S6, Supporting Information), namely, a bright-dark contrasted cubic pattern and a closely packed cubic pattern. “Close-up” observation of the cubic AuNP arrangement showed interdigitated bright and dark contrasts with bright spots reflecting vertically stacked AuNPs alternating with thinner stacking (Figure S7, Supporting Information).

Self-assembly did not occur on the SiN-30C surface. Instead, we observed a random attachment of the AuNPs in a single horizontal layer of lower density than the other samples (Figure S8, Supporting Information). Changing the thickness of the molecular surface coating apparently altered the strength of the substrate–AuNP interaction. Thicker coatings likely reduce substrate–AuNP attraction and allow solvent molecules to move between particles and substrate. Note that the weak interactions between the particles and substrate at thicker surface coatings were only observed in situ and not in the dried samples. Drying the sample led to different particle packings (Figure S9, Supporting Information) than those found in liquid, and the images did not contain the extended areas covered with dqc or bcc symmetry, as seen in Figure 2.

The aforementioned experiments were carried out in cyclohexane, a solvent with a dipole moment $\mu$ close to zero. In toluene ($\mu = 0.31$ D), different observations were made. The dqc packing was observed for SiN-P (Figure S10a, Supporting Information) instead of hcp. It is conceivable that an interfacial toluene layer formed by polarization of the toluene molecules at the substrate.\textsuperscript{[22]} The polarized liquid layer presumably reduced the interaction between AuNP and substrate, which is consistent with the observation of a dqc packing for SiN-6C (Figure S10b, Supporting Information). The bcc symmetry was not found for SiN-18C, but instead random sparse AuNP deposition was observed (Figure S11, Supporting Information), indicating that the combination of the thick surface coating and the polarizable solvent reduced the particle-substrate interaction sufficiently to render self-assembly thermodynamically unfavorable.

### 2.3. 3D Models of the Superlattices

The 3D packing geometry was inferred from STEM intensity levels that scale approximately linearly with the number of Au atoms crossed by the beam,\textsuperscript{[26]} so that discrete steps in signal intensity indicate differences in stacking heights of AuNP layers. The hcp geometry on SiN-P (Figure 2b) contained a second layer of AuNPs located between three first-layer AuNPs. For the dqc ring on SiN-6C, the central AuNP (bright spot) was surrounded by twelve other AuNPs, resulting in a circular distribution of the particles (Figure 2c). Analyzing several close dqc rings, such dodecahedral geometry was consistent. The dqc ring can be envisioned as two overlapping hexagons with a 30° rotation. The bright–dark contrasted cubic geometry on SiN-18C (Figure 2e) corresponded to the bcc structure, where the first and the third layer AuNPs fully overlapped. The second layer of AuNPs can be envisioned as the center particle of the cube.

LP-STEM was used to visualize lateral AuNP positions, which allowed accurate measurement of the spacing between neighboring particles in the vertical projection of the plane parallel to the substrate’s surface, hereafter referred to as the center-to-center (C-C) distance. A measurement of 25 AuNP C-C spacings (Figure S12, Supporting Information) indicated that hexagons in hcp (on SiN-P surface) exhibited a C-C spacing of $10.3 \pm 0.5$ nm, while the spacing for dqc hexagons amounted to $11.1 \pm 0.5$ nm. The gap between the two AuNPs in the hcp structure was 27% smaller than the thickness of the oleylamine ligand shell (2 nm in length) but was only 8% smaller for dqc. The reduced C-C spacings likely resulted from combined bending and interdigitating of the oleylamine of neighboring AuNPs, as previously investigated in simulations.\textsuperscript{[40]} The
measured AuNP C-C spacing from the bcc structure observed for the SiN-18C surface amounted to 12.1±1.0 nm, consistent with fully extended and separated oleylamine shells. The particle packing density thus decreased in discrete steps (hcp, dqc, bcc) with decreasing particle-substrate interaction.

2.4. Role of Particle Faceting in Self-Assembly

The dependence of the self-assembled superlattices on SAM thickness indicates that short-range interactions between AuNPs and the SiN substrate dominated self-assembly. We therefore asked whether, in this size range, it is correct to consider the particles as perfect spheres, as is usually done in theoretical descriptions of particle-substrate interactions,[7b] or whether the faceted structure of the AuNP possibly also affected self-assembly, an effect that has been previously reported for semiconductor nanoparticles.[6] High-resolution STEM images in the dry state revealed the faceted surface of the AuNP cores (Figure S13, Supporting Information). For this type of AuNP of sizes approximately 8 nm, a 3D structure is thermodynamically favored that consists of two lattice planes (100) and (111) exposed at the surface forming truncated octahedra.[23] The surface energy of an Au fcc facet (100) (0.918 J m⁻²) is 14% higher than that of a (111) facet (0.790 J m⁻²), implying that the (100) planes at the AuNP surface host more unsaturated bonds and are thus more prone to ligand capping,[24] leading to a higher capping density.[25] Note that the same effect can also be used to selectively remove ligands from specific facets and thus induce AuNP adherence following the self-assembly process.[26] Therefore, the oleylamine density on (100) was presumably higher than that on (111) surfaces, as depicted in Figure 3a.

![Figure 3](https://www.advancedsciencenews.com)

**Figure 3.** Schematic illustration of facet-dependent AuNP ligand distribution and self-assembly orientations. a) Schematic presentation of the (100) and (111) facet planes of AuNPs with different oleylamine ligand densities. b) Bottom view and 3D representation of AuNPs landed on SiN-P, SiN-6C and SiN-18C surfaces. The AuNPs are from the same atomic model only differed by orientations. The (111) facet faces the SiN surface to form a stable structure. c) Schematic illustrations of the AuNPs assembled on SiN with different coatings. The blue solid lines drawn on the bottom view of the patterns represent planes (P_A, P_B, and P_C) parallel to the viewing direction and are correspondingly shown in the bottom side views. The AuNP C-C spacing variations in the side view correlate with those observed from the experiments.
AuNPs in close proximity to a charged surface are attracted by van der Waals interactions, and in addition, the polar substrate induces an electric dipole in Au that leads to electrostatic attraction. The substrate–NP attraction increases with decreasing distance. We assume that the distance between the NP and the surface was the shortest for NPs that had a (111) facet facing the substrate, because this facet has a lower ligand density and greater ligand shell compressibility than (100) (Figure 3b). NPs landing with their (111) facet on the SiN-P substrate would thus be energetically preferred over those landing with the (100) facet. The smallest C-C spacing occurred when the sideward facing (100) facet closest to the substrate was oriented toward the sideward facing (111) facet of the adjacent NP, as depicted in the side view projection in Figure 3c. This may contribute to the formation of the hcp packing that was observed for SiN-P (Figure 2a) with the thinnest surface coating. On SiN-6C, AuNPs presumably also landed on the (111) facet but now with a somewhat larger distance to the substrate than for SiN-P due to the additional spacing from the substrate monolayer coating, resulting in a reduced substrate–NP attraction. For this sample, the experiments showed a dqc symmetry (Figure 2d) with increased C-C spacing. A possible explanation for the increased in-plane spacing is that the adjacent sideward facing (100) facets of the adjacent NPs now face each other (Figure 3c). On SiN-18C, the alkyl monolayer was nearly as thick as the AuNP oleylamine shell. At this separation, the substrate–Au attraction was the lowest. Possibly, a rebalancing of forces took place compared to SiN-P and SiN-6C in such a way that the (100) facets of neighboring AuNPs now face each other, which is only possible if the NPs landed on the substrate on their (100) facets (Figure 3c), giving rise to the experimentally observed bcc symmetry and the largest C-C spacing. We thus formulate the hypothesis that a change in the landing facet from (111) to (100) changes the self-assembled pattern from either hcp or dqc to bcc. The above considerations suggest that the different geometries observed in our experiments (Figure 2) are a result of changes in facet-dependent interactions between the AuNPs and the various SiN substrates.

2.5. Langevin Dynamics Simulations of the Self-Assembly Process

To gain an understanding of the driving forces responsible for stabilizing the experimentally observed structures, a complex interplay of multiple factors and potentials must be examined. For this purpose, we constructed a range of models and studied their self-assembly subject to Brownian motion using Langevin dynamics simulations, thereby separately investigating the influences of AuNP faceting, ligand coverage, electrostatic dipoles induced in the AuNPs, and their vdW attraction with the substrate. Our models for the AuNPs consisted of a shell of overlapping beads forming a rigid body meant to represent the outer surface of the oleylamine ligand shell that surrounded the truncated octahedral AuNP core (Figure 4a). These beads interacted with each other and the substrate surface via a Lennard-Jones (LJ) potential, which we used to describe the AuNP–AuNP and AuNP–SiN vdW interactions. The total LJ attraction between two approaching NPs in our simulations is similar in strength to the vdW attraction between two 8.3 nm spherical gold cores separated by a surface spacing of ≈2 nm, which is the estimated gap between cores in our experiments (Figure S17a, Supporting Information). The LJ interaction between the NP and substrate is approximately a factor of six stronger than that of NP–NP attraction and similar in strength to the vdW attraction between an 8.3 nm Au sphere and a SiN substrate at a separation of 1.5 nm (Figure S17b, Supporting Information). Self-assembly in the simulations was initiated by decreasing the temperature, which is equivalent to increasing the interaction energies at constant temperature (see Supplementary Information for further details, including how the simulation units were converted to real units).

The influence of the AuNP shape on the self-assembly process was studied first in bulk solution by considering particles with various degrees of faceting, controlled by a shape parameter s. We defined shapes ranging from truncated octahedral (s = 0) to spherical (s = 1) via an intermediate rounded faceted (s = 0.65) particle. Of these, only the spherical and rounded faceted particles were able to form the experimentally observed fcc structure in bulk solution, that is, in the absence of any substrate influence (Figure S14, Supporting Information). This outcome shows that the ligand shell has a rounding effect on the particles, which is consistent with simulations of similar NPs using a model that includes explicit ligand molecules.[27] Self-assembly in the bulk of the s = 0.65 particles occurred when the attraction energy between the particles was ≈3kT at contact, consistent with experimental results showing that stable AuNP dispersions were obtained at room temperature (Figure S1b, Supporting Information).

Simulations were then conducted that also included interactions at the surface. The presence of the substrate induced surface-driven self-assembly for the rounded faceted particles (s = 0.65) at room temperature (Figure 4b), corresponding to ≈10% weaker NP–NP attraction than needed for bulk assembly. Different assembled patterns were formed by perfectly spherical particles (s = 1) and rounded faceted (s = 0.65) particles. For perfectly spherical particles, the assembled structure was always hcp (Figure S15, Supporting Information). In comparison, assembly of the rounded faceted particles was better able to explain the experimental results: the hcc superlattice observed on SiN-18C formed when the (100) facets were preferentially attracted to the substrate (Figure 4d and Figure S15, Supporting Information), whereas the hcp superlattice observed on SiN-P formed when the (111) facets were preferentially attracted to the substrate (Figure S15, Supporting Information), confirming our hypothesis of the switch between hcp and hcc depending on the landing facet illustrated in Figure 3c. A change in the preferred landing facet on SiN-18C would be consistent with previous evidence for vdW attraction between dense ligand layers in solution.[10]

We also considered how self-assembly of the rounded-faceted AuNPs would be affected by polarization induced by the SiN-P and SiN-6C substrates. Polarization of the Au cores was modeled by a dipole p = d·q, represented by two opposite point charges ±q placed symmetrically under opposite (111) facets and separated by a distance d equal to the diameter of the AuNP core (see Figure 4c and Supplementary Information). The simulated assembly showed hcp symmetry for dipoles as...
large as 459 D (Figure S16a, Supporting Information), with a transformation to \( \text{sh} \) packing at higher polarization (Figure 4c; Figure S16b, Supporting Information). It is likely that this transition occurs experimentally at smaller dipole magnitudes, as the simple dipole model that we have used does not account for the smeared nature of the induced surface charges and collective polarization effects between multiple particles.[28]

In addition, we considered vdW attraction between the substrate and particles not directly in contact with it by adding a force \( f_{\text{vdW}} \) perpendicular to the substrate) to the center-of-mass of all particles within a range of \( \sim 2d \) from the substrate. Including vdW attraction, the \( \text{sh} \) structure was preserved up to \( f_{\text{vdW, real}} = 5.9 \times 10^{-13} \) N (Figure S16b,c, Supporting Information), but transitioned to \( \text{hcp} \) at \( f_{\text{vdW, real}} = 7.8 \times 10^{-13} \) N (Figure 4f and
Figure S16d, Supporting Information). Increasing \( f_{\text{dW}} \) in our simulation corresponds to increasing the Au-SiN attraction, which is expected during the shift from SiN-6C to SiN-P. Compared with theoretical calculations (Figure S17c, Supporting Information), the increased \( f_{\text{dW}} \) translates to a reduced SiN–AuNP spacing of 0.68 nm, which is approximately the length of a 6C alkyl chain. These results suggest that the AuNPs may be highly polarized on both SiN-P and SiN-6C but that stronger attraction to the substrate stabilizes the hcp superlattice on SiN-P, while weaker attraction to SiN-6C results in more \( sh \) packing. Although our simulations did not form the \( dqc \) rings shown in Figure 2d, it is likely that the crossover regime between the hcp and \( sh \) structures is sensitive to factors not considered in our current models, such as variations in core faceting, the ability of the ligand shell to deform, and collective polarization effects.\(^{[29]}\)

3. Conclusion

We have shown that short-range interactions dominated the assembly of oleyamine-capped AuNPs on SiN. The assembly orientation of the AuNPs seems to be facet-dependent for smaller core-substrate distances and a key factor driving the self-assembled superlattice geometry, as was confirmed by Langevin dynamics simulations. The fundamental mechanism of this observation is related to the surface energy differences of Au facets, that is, (100) and (111), which adsorb ligands at different densities. Depending on the strength of the dipole–dipole interactions and vdW forces, the AuNPs landed on a different facet, resulting in fundamentally different superlattice symmetries, including hcp, \( sh \), \( dqc \), and bcc patterns. Some of the lattices existed only in the liquid and changed their geometry during drying, highlighting the risk of preparation artifacts and the need for in situ studies. Self-assembly of colloidal materials in liquid possesses subtle behaviors depending on the (sub)nanometer-scale shapes of the involved NPs, as well as the ligand’s flexibility in forming versatile self-assembled structures. The nanoscale morphology of the involved materials is thus a key factor in understanding particle–particle and particle-substrate interactions and should thus be included in self-assembly design.

4. Experimental Section

Preparing the Microchip Surfaces: The SiN surfaces of the microchips were chemically modified to tune the particle-substrate spacings. The microchips (Protochips Inc., NC, USA) were washed with acetone and then ethanol, each for 2 min (acetone and ethanol were high pressure liquid chromatography grade, Sigma–Aldrich, Germany) to remove the surface protection coating.\(^{[30]}\) For microchip handling, a straight carbon-tip tweezer was used to avoid chipping the edge of the microchip. Care was taken to avoid touching the SiN surface. The washing procedure was carried out for four large microchips and four small microchips, which were combined in 50 mL of each solvent. Transfer from acetone to ethanol was carried out such that the surface of the microchip remained wet. The microchips were then placed on a cleanroom cloth, dried in air for 10 min, and stored in a plastic box.

To render the SiN surfaces hydrophilic, the microchips were plasma treated (plasma reactor Model 950 Advanced Plasma System, Gatan, Inc., USA) for 5 min in a flow of Ar (35.0 sccm) and \( O_2 \) (11.5 sccm) with a working power of 1000 W. Alkyl silane grafting was carried out on microchips by placing two small and two large microchips in a sealed glass bottle filled with 40 mL of alkyl silanes in dry toluene (2.2 \( \times 10^{-3} \) m) for 19 h, a procedure known to cause minimal damage to the SiN.\(^{[31]}\) The silanes formed covalent bonds with hydroxy groups of the plasma-treated surface, and an alkyl monolayer assembled. In this work, alkyl silanes of different carbon chain lengths were used, including trichloro(hexyl)silane (6C), octadecyltrichlorosilane (18C), and triacyctyltrichlorosilane (30C) (all from Sigma–Aldrich, Germany). After surface treatment, the microchips were transferred to 50 mL of the same solvent and gently shaken for 5 min to remove unattached silanes. Transferring from the toluene solution, subsequent washing was carried out in pure acetone and ethanol with the same procedure as the protection coating removal mentioned above. After drying the microchips in an enclosed dust-free hood, the modified microchips were stored in a vacuum container before use.

Synthesis of AuNPs: The Au NPs were synthesized using a modified protocol based on Wu and Zheng.\(^{[32]}\) Specifically, a mixture of 8 mL of toluene (puriss \( \geq 99.7\% \)), 8 mL of oleylamine (technical grade, 70%), and 100 mg of HAuCl\(_4\)·H\(_2\)O was stirred at 20 °C and 500 rad min\(^{-1}\) for 1 min under argon atmosphere. Afterward, 40 mg of tert-butylamine borane (ABCRI, 97%), which was dissolved in 2 mL of toluene and 2 mL of oleylamine, was added to the solution. The color of the solution immediately turned dark purple. After stirring for 60 min at 20 °C, the nanoparticles were purified once by precipitating with 30 mL of ethanol and centrifugation at 4000 rad min\(^{-1}\) for 5 min. The precipitated nanoparticles were redispersed in either 20 mL of toluene or cyclohexane (puriss \( \geq 99\% \)).

Sample Preparation for LP-STEM: To load the microchips in the liquid-flow holder (Poseidon Select, Protochips Inc., NC, USA), a straight carbon-tip tweezer was used. First, the small bottom microchip was placed flat on the bottom O-ring. Then, a small droplet of AuNP solution (0.8 \( \mu \)L for AuNP–cyclohexane and 0.4 \( \mu \)L for AuNP–toluene) was added to the surface of the small microchip. More cyclohexane was used than toluene since cyclohexane evaporated faster than toluene. The amounts of liquid used were sufficient to avoid drying during assembly of the liquid cell. This operation was conducted under a binocular microscope for precise droplet placement. The large microchip was placed into the holder within 10 s to minimize solvent evaporation, thereby sandwiching the liquid sample between both microchips. Last, the holder cap was gently placed and tightened using a torque screwdriver. A torque limit of 13 mN m was used, and each of the three screws was tightened in a stepwise manner to maintain uniform loading. After sealing, the window area of the microchip was inspected under an optical microscope for potential liquid leakage. To further inspect for leakages, the holder was transferred to a vacuum chamber (HiCube 80 Classic, Pfeiffer Vacuum GmbH, Germany) for examination where the vacuum pressure should reach 6 \( \times 10^{-4} \) mbar or below. Each self-assembly experiment was repeated three times where the pattern variation was consistent.

Liquid-Phase Scanning Transmission Electron Microscopy: Experiments were carried out using a transmission electron microscope equipped with a cold-field-emission gun (JEM-ARM 200F, JEOL, Japan) and an STEM probe corrector (CEOS GmbH, Germany). The electron beam energy was 200 kV. The annular dark-field detector was used with an 8 cm camera length. For scan settings, a 4C spot size and beam aperture of 20 \( \mu \)m were used, which gave a probe current \( I_p = 80 \) pA. The above parameters rendered an electron probe convergence semicircle \( \alpha = 13.2 \) mrad, a detector opening semicircle \( \beta = 68 \) mrad reflecting the detector active area, and a semicircle \( \beta = 43 \) mrad reflecting the diameter of the hole through which the beam passes for measuring the current and calculating the liquid thickness. The images were acquired with a pixel dwell time \( t = 2 \) \( \mu \)s and a size of 1024 \( \times 1024 \) pixels. The pixel size \( s_p \) varied with the magnification. To limit electron beam exposure to the samples as much as possible (>200k magnification), the image focus and stigmator were adjusted for optimization in one area, and the beam was blocked. After slightly moving the stage to an unexposed
area, the beam block was removed, and the image was acquired immediately. The electron flux was approximated by \( e_f = \frac{i_f}{e-s_f^2} \), where \( e \) is the elementary charge. The electron dose \( eD = \tau \times e \). For the LP-STEM images presented in this work, it was verified that the liquid enclosures were indeed filled with liquid and the samples thus fully immersed from measuring the liquid thickness (Table S3, Supporting Information).

**Longsevin Dynamics Simulations:** All simulations were carried out in an NVT ensemble using LAMMPS.\(^{[30]}\) Periodic boundary conditions were applied in the \( x \) and \( y \) directions. In the vertical direction, there are two walls that keep the particles inside the box: a bottom flat wall, representing the substrate, which interacts with particle beads via the Lennard-Jones potential, and a top flat wall, which interacts with particles via the repulsive Weeks–Chandler–Andersen (WCA) potential.\(^{[30]}\) In all cases, at least three simulations with different initial configurations (the NPs were randomly placed in the simulation box) were conducted, and consistent results were obtained. Complete simulation procedures, including details of the models used and conversion to real units, can be found in the supplementary information.

**Statistical Analysis:** AuNP self-assembly experiments were performed for each modified surface on three different samples. At least 30 images from each surface type at different locations were recorded to investigate the formed superlattice structures and their homogeneity (Table S1, Supporting Information). On each image, areas corresponding to each superlattice pattern were measured using the Selection and Analyze-Measure tools in ImageJ. For the AuNP center-to-center (C-C) distance, transformation, signal intensity measurement, and interparticle distance analysis.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Author Contributions

All authors designed the experiments and contributed to the writing of the manuscript. A.B. and B.K. conducted the experiments, and Y.L. conducted the simulations. A.B. and Y.L. analyzed the data.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

gold nanoparticles, liquid–solid interfaces, nanoparticle faceting, self-assembly, superlattices, surface modification

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