Hierarchical self-assembly of 3D lattices from polydisperse anisometric colloids

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Colloids are mainly divided into two types defined by size. Micron-scale colloids are widely used as model systems to study phase transitions, while nanoparticles have physicochemical properties unique to their size. Here we study a promising yet underexplored third type: anisometric colloids, which integrate micrometer and nanometer dimensions into the same particle. We show that our prototypical system of anisometric silver plates with a high polydispersity assemble, unexpectedly, into an ordered, three-dimensional lattice. Real-time imaging and interaction modeling elucidate the crucial role of anisometry, which directs hierarchical assembly into secondary building blocks—columns—which are sufficiently monodisperse for further ordering. Ionic strength and plate tip morphology control the shape of the columns, and therefore the final lattice structures (hexagonal versus honeycomb). Our joint experiment–modeling study demonstrates potentials of encoding unconventional assembly in anisometric colloids, which can likely introduce properties and phase behaviors inaccessible to micron- or nanometer-scale colloids.
Anisometry is a potent strategy for biological and artificial building blocks to integrate the merits of both micron- and nanometer-scale dimensions. For example, bundling of anisometric tropocollagen helices into the fibrous protein collagen allows multiple building blocks to work in concert under loads, giving collagen its exceptional elastic energy absorption. Nanoscale DNA strands can be engineered to braid into micron-scale filaments to build programmed architectures. Similarly shaped synthetic nanowires can serve as ideal energy transport materials to direct longitudinal conduction of quantum particles such as electrons, phonons, and photons. However, despite extensive work on micron-scale colloids and nanoparticles, anisometric colloids as a promising and emergent particle type are still greatly underexplored. Most work has focused on one-dimensional anisometric building blocks (filaments, tubes, wires, etc.) [1, 4-6]. Recent work by our group and others explored shapes like anisometric metallic plates, which were shown to be great candidates for self-assembly studies. On the one hand, a nanoscale thickness (and therefore low gravitational drag) allows the plates to diffuse freely in solution, which enables their assembly in three dimensions (3D). In comparison, previous work on micron-scale colloids has required either a precise match with solvent density or an external field to build 3D structures against gravity. These experimental requirements pose limitations which are in principle irrelevant here (Supplementary Note 1). On the other hand, a micron-scale basal plane makes plates visible under optical microscopy, making it possible to track their translational and rotational motions one-by-one and thus elucidate the assembly dynamics from real time and real space imaging, which was not accessible in nanoplate systems characterized previously by small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), or electron microscopy with dried samples. In comparison, although nanoparticles can assemble into 3D structures, understanding and predictive engineering of their assembly pathways have been challenging due to the technical difficulty in direct imaging of such processes in solution. However, despite the great advantages from anisometric plates, the observed assembly into one-dimensional lamellar superlattices from these plates is the same behavior seen in nano-sized metallic plates, the potential of anisometry to enrich phase behavior was not fully harnessed.

Here we show that the anisometry of silver plates (having a micron-scale basal plane and a nanoscale thickness), when utilized meticulously, opens the design space of colloidal self-assembly to a regime not easily accessible before. Anisometry not only brings the technical ease for studying self-assembly, it also renders strongly directional interactions that favor hierarchical self-assembly along one plate axis at a time. In this way, the initial products in our system, hereafter referred to as “columns”, embody the concept of secondary building blocks in molecular crystals, which can further assemble into ordered 3D lattices due to a size-focusing effect (an effective narrowing of the building block size distribution). The apparent shape of columns can be predictively manipulated by ionic strength or the extent of plate tip truncation, which leads to distinct final lattice structures. Such unexpected 3D lattices have not been observed in previous systems of metallic nanoparticles. Our study demonstrates the unique secondary building block engineering opportunity enabled by anisometry as well as the greatly enriched phase behaviors of anisometric colloids, which opens doors to incorporating their unique mechanical, optical, and electronic properties into 3D assemblies.

**Results**

**Anisometric plates self-assembly in 3D.** Anisometric silver plates studied in this work have a triangular basal plane and tunable extent of tip truncation (Fig. 1a, Supplementary Fig. 1, Supplementary Table 1) that we later show as critical to the selection of final lattice structures. The plates were colloidally synthesized following literature methods of seeded growth with slight modification. Tip truncation results from the formation of alternating sides during the kinetic expansion of the basal plane, as explained by Lofnon and Sigmund in the silver halide model. The first plate type we studied has a long side length \( L = 1.49 \pm 0.24 \) µm, a short side length \( L' = 0.79 \pm 0.27 \) µm, and a plate thickness \( d_{\text{plate}} = 35 \pm 5 \) nm (Fig. 1a, Supplementary Fig. 1). The aspect ratio of the plates, defined as the ratio of circum-scribed diameter to the thickness, is as high as ~66. Plates are coated with negatively charged carboxylate-thiols and thus electrostatically repel each other when dispersed in deionized water (Fig. 1a, Supplementary Note 2). The plates exhibit vivid in-plane and out-of-plane rotations in 3D as observed under optical microscopy, with a vertical fluctuation height as much as 11 times the plate thickness (Supplementary Fig. 2a, b, Supplementary Note 1). Such out-of-plane rotation in 3D, given one order of magnitude difference between the densities of silver and water, is possible due to the nanoscale thickness.

Self-assembly of the dispersed plates was triggered by increasing the ionic strength (0.5 mM NaCl), leading to the formation of standing column secondary building blocks by face-to-face plate stacking (Fig. 1b, Supplementary Fig. 2c, Supplementary Movie 1). The column geometry was verified under optical microscopy, as rotating columns exhibit light, rectangular projections while lying on their sides and dark, polygonal projections while standing vertically on the substrate (Fig. 1c, Supplementary Movie 2). At this ionic strength, van der Waals attraction \( E_{\text{vdW}} \) between adjacent plates overcomes electrostatic repulsion \( E_{\text{el}} \), and because the basal plane has a ~63 times larger interacting area than the plate side, face-to-face stacking into columns is favored over lateral assembly. Specifically, based on the pairwise interaction \( E_{\text{out}} = E_{\text{vdW}} + E_{\text{el}} \) we computed following a discretized model\(^{10, 41}\), the face-to-face stacking as observed in experiments has an \( E_{\text{out}} \) minimum of ~6.1 \( k_B T \) (Fig. 1d, Supplementary Fig. 3, Supplementary Table 2), while the side-by-side configuration is not as stable, with a negligible \( E_{\text{out}} \) minimum of ~0.02 \( k_B T \). Face-to-face stacking of plates within the columns was further verified by SAXS, where the measured face-to-face spacing between adjacent plates, the \( d \) spacing, is consistent with that predicted by both the analytical and discretized models for plate–plate interactions (Supplementary Fig. 4, Supplementary Table 3). Based on the \( d \) spacing, one column is composed of ~15 plates (Supplementary Fig. 2d, e). The column structure was also observed in our earlier work on plates that have a smaller basal plane area (0.90 µm\(^2\) versus 3.27 µm\(^2\) here). The key difference is that, due to their larger basal plane area, the columns in this work experience enhanced van der Waals attraction with the substrate and larger gravitational force, so the columns prefer to stand vertically on the substrate (Supplementary Fig. 2c, Supplementary Note 3), facilitating the subsequent lateral assembly of columns as secondary building blocks.

**Ordering from polydisperse plates via size-focusing.** The standing columns further assemble as their concentration increases into an ordered hexagonal lattice due to a size-focusing effect in the columns (Supplementary Movie 3). This size-focusing effect is a direct result of the plate anisometry. Figure 1e, f summarizes the overall trend as we tilt the microscopy chamber slightly to concentrate the columns. The fast Fourier transform of the final equilibrated structure (FFT, Fig. 1e, inset) reveals a global hexagonal order. Our tracking of adjacent columns in the
Hierarchical self-assembly of polydisperse, anisometric plates into a 3D lattice. **a** Top: schematics of anisometric silver plates (green) coated with thiolated COO⁻ ligands (blue) and their directional attractions (red arrows). Bottom: a representative atomic force microscopy (AFM) scan over an anisometric plate. The color bar represents height. Scan area: 5 µm × 5 µm. **b** Schematics describing the hierarchical building process: plates first stack into columns (yellow arrows denoting the random orientations of the plates), which then assemble into a hexagonal lattice. The graphs below show the distribution of the long side length of plates (left, green curve) and that of column projection diameter (right, blue curve). The L distribution was rescaled so that L and D have the same value (2.36 µm) for direct comparison. **c** Time-lapse optical microscopy images and schematics showing the lying and standing orientations of the same rotating column. **d** Theoretical calculations of the net pairwise interactions \( E_{\text{net}} \) of two plates in the face-to-face (red circles) and side-by-side (black circles) configurations as a function of the plate–plate distance \( d \) (labeled in inset schematic). **e** An optical microscopy image showing a hexagonal lattice, overlaid with tracked trajectories of the central positions of the column projections. The image was processed as detailed in Supplementary Fig. 5 and Supplementary Note 4. The bottom right inset is a fast Fourier transform (FFT) pattern of the image. **f** Optical microscopy images showing column arrangements as their concentration increases (from left to right). Ionic strength in **c–f**: 0.5 mM. The schematics were not drawn to scale. Scale bars: 1 µm in **c**, 5 µm in **e**, 3 µm in **f**.

Lattice (traces labeled in Fig. 1e) shows highly localized vibrations at the lattice sites, validating the lattice stability. Two details are noted in the hexagonal lattice formation. First, the plates are polydisperse (about 16% based on \( L \), 34% based on \( L' \)) because the growth of micron-sized particles from nano-sized seeds is highly susceptible to local fluctuations in solution, as reported previously. This polydispersity is usually considered too high for forming an ordered crystal (for example, <12% polydispersity is required for spheres to crystallize). However, the secondary building blocks of columns average their sizes due to plate stacking, thereby rendering them generally reduced polydispersity (8%) to assemble into an ordered lattice (Fig. 1b). Such a size-focusing effect can potentially account for the formation of similar 3D lattices from polydisperse Al(OH)₃ nanoplates presented in earlier work, where ensemble structure was characterized by SAXS. This effect which enables ordered assembly from polydisperse building blocks is also reminiscent of the monodisperse superspheres formed from polydisperse CdSe nanoparticles, but was achieved here via hierarchical averaging, not self-limiting clustering which requires an intricate balance of competing forces. Second, the columns are otherwise dispersed at low or intermediate column concentrations (Fig. 1f, Supplementary Fig. 6, Supplementary Movie 4), indicating a weak or negligible attraction between the columns at this ionic strength. The weak attraction is further verified as the columns were observed to diffuse close into contact and then apart due to the absence of strong attraction (Supplementary Fig. 6a, b), such that they only crystallize into ordered lattices when their concentration is sufficiently high. The ordered hexagonal lattices are observed in multiple plate samples of different sizes (Supplementary Fig. 7), further demonstrating the robustness of the 3D hierarchical assembly. The 3D nature of the assembled structures is also verified by scanning electron microscopy (SEM) imaging (Supplementary Note 5), where layers of plates are clearly shown to stack into laterally interacting columns (Supplementary Fig. 8).

A close investigation into the relative rotations of plates in the columns further reveals how the effective shape of columns is reduced into monodisperse, radially symmetric circular columns. As shown in Fig. 2a and Supplementary Figs. 9 and 10, the constituent plates in a column rotate relative to each other...
(Supplementary Movie 5) so that the projections of columns dynamically vary. Plates at the first few layers in the column are clearly identified based on their contrast difference under optical microscopy (Supplementary Movie 5). The outlined contours of the column projections were color-coded according to the local curvature of the projection contours tracked at 0, 0.2, and 0.5 s in a. c Orientations of two plates (one in gray, the other in black) in a pair of nearest neighbor columns inside the lattice over time, and time-lapse optical microscopy images with the plate orientations labeled in yellow. The measurement errors are ±5°. d Time-lapse optical microscopy images (top) and corresponding Voronoi cell representations (bottom) of the hexagonal lattice, showing the annealing of imperfectly coordinated sites. The arrows in the top panel are color-coded by the velocity magnitude $|\mathbf{v}|$ of columns calculated over a period of 0.7 s (12 frames). The color of each Voronoi cell denotes the number of nearest neighbors $Z_j$ per column $j$. e Radial distribution function of the lattice in experiment (green curve) and that of an ideal hexagonal lattice (gray lines). The inset defines the center-to-center distance $r$ between columns. A $D$ value of 2.36 $\mu$m is used in the plot. f The local order–local density $\langle |\psi_0|, \rho_j \rangle$ histogram based on single column tracking of the hexagonal lattice (32 frames in Supplementary Movie 3). Here $|\psi_0| = \sqrt{\sum_{k=1}^{3n} \exp(6\beta_k)}$, where the summation goes over all the nearest neighbors of column $j$, and $\beta_k$ is the angle between the bond linking column $j$ and its $k$th neighbor and an arbitrary reference axis\(^{46,47}\). Ionic strength: 0.5 mM. Scale bars: 1 $\mu$m in a; 2 $\mu$m in c, d.
Fig. 3 The effective shape of columns modulated by ionic strength or plate tip truncation. a Schematics (left) and SEM images (right) showing plates of a systematically varying extent of truncation $m$ (defined as $L/L$). The top right SEM image shows the plates used in the hexagonal lattice. The corresponding truncation distributions are shown in Supplementary Fig. 13. Scale bars: 1 µm. b A graph showing how the computed pairwise interaction $E_{\text{tot}}$ between two stacked plates ($m = L/L = 0.53$, corresponding to the plates used for hexagonal lattice) changes as a function of $\Delta \theta$ at different ionic strengths (from top to bottom: 0.5, 1, 1.5, 2, and 2.5 mM, respectively). Note that 0.5 mM is used in the hexagonal lattice assembly. c Relative probability distributions of $\Delta \theta$ based on a Boltzmann distribution argument at different ionic strengths, computed from the interaction energy plot in b (color coded the same as in b). The inset schematics show misaligned plate orientations inside column (left) at low ionic strength (0.5 mM) and well-aligned plate orientations (right) at high ionic strength (2.5 mM). d A graph showing how the computed pairwise interaction $E_{\text{tot}}$ between two stacked plates changes as a function of $\Delta \theta$ at different extent of truncation $m$ as labeled. Here the calculations are conducted at a fixed basal plane area (3.27 µm²). Ionic strength: 0.5 mM. e Pairwise interaction strength as a function of $\Delta \theta$ and truncation $m$ at their energy minimum spacing $d$. Ionic strength: 0.5 mM.

Modulating the effective shape of columns. Having elucidated that the circular shape of columns leads to hexagonal lattices, we next demonstrated that the effective shape of columns can be controlled by changing the ionic strength or the extent of plate tip truncation, potentially leading to different lattice structures. Here we define a parameter $m$ as the ratio between the short ($L'$) and the long ($L$) side lengths of a plate, to quantify the extent of tip truncation. As shown in both the schematics and SEM images (Fig. 3a), an $m$ value of 0 corresponds to a triangular plate with sharp tips and 1 to an equilateral hexagonal plate. Regarding the ionic strength effect, given the same type of plates as studied in the above (the plates that are assembled into a hexagonal lattice), we calculated the interactions $E_{\text{tot}}$ between a stacked plate pair with varying relative in-plane orientations $\Delta \theta$ at their energy minimum spacings, as a function of ionic strength (Fig. 3a, b; see details in Methods). At a relatively low ionic strength (0.5 mM, the experimental condition for forming hexagonal lattice), $E_{\text{tot}}$ is weakly dependent on $\Delta \theta$ over a range of $-60^\circ$ to $60^\circ$. Based on a Boltzmann distribution argument (relative probability, $p_{\text{rel}}(\Delta \theta) = e^{-\Delta E/k_B T}$, where $\Delta E$ is the $E_{\text{tot}}$ difference for two plates at different relative orientations, see Fig. 3c), large plate–plate relative rotations are allowed with low energy penalty. This prediction is also consistent with our experimental observations of fast relative rotations of plates at this ionic strength condition (Fig. 2a, b). The interaction profile becomes increasingly steeper with respect to plate relative rotation as ionic strength increases, restraining the relative rotations between adjacent plates so that the plates within the columns favor aligned orientations (Fig. 3c). We verified this trend in experiments at high ionic strength (2.0 mM). At this ionic strength, the electrostatic repulsion is more screened, leading to a decreased separation between plates in the columns, higher enthalpic penalties for plate relative rotation, and therefore dampening of plate relative rotations as well as a significant increase in the lateral attraction between columns. Irregular, fractal-like assemblies from columns were observed from the same plate sample at high ionic strength (2.0 mM; Supplementary Fig. 12). In addition, plate tip truncation also drastically changes the allowed relative rotations of plates and thus the effective shape of columns. For pairwise interaction $E_{\text{tot}}$ calculated at a constant ionic strength and a constant basal plane area, but at varying $m$, we find a more hexagonal shape (a larger $m$) renders a flatter interaction profile over different $\Delta \theta$ values (Fig. 3d, e). The plates with a more triangular shape (a smaller $m$), on the other hand, have a steeper potential well disfavoring relative rotations between plates. This interaction profile, on the column level, maintains the generic three-fold symmetry of triangular plates instead of a smeared-out circular shape. This detail of tip truncation was not recognized in the previous literature², due to the lack of importance in inter-column interactions in those systems.

Experimental realization of 3D honeycomb lattice. Finally, we experimentally realized the triangular columns predicted above, and in doing so observed a different final assembly: honeycomb,
not hexagonal, lattice domains are formed upon decreasing the extent of plate tip truncation and increasing the ionic strength (Fig. 4a). We synthesized less truncated triangular plates while maintaining anisometry ($\bar{m} = 0.17$, Fig. 4a, Supplementary Fig. 14). As shown in Fig. 4b, these plates assemble into columns at increased ionic strengths (3.2–5.5 mM). The column projections are mostly triangular, with the contoured local curvature distributions staying roughly constant over time (Fig. 4b, Supplementary Movie 5). Such distributions suggest that the stacked plates within the columns remain aligned, with negligible relative plate rotation. This observation is consistent with our interaction modeling (Fig. 4c), which shows that even a small relative plate rotation of 20° can be strongly disfavored due to an interaction energy penalty as high as $3 k_BT$. The disfavoring of plate misalignment in the columns leads to a triangular column projection, which encodes an assembly symmetry distinct from the isotropic, circular ones studied above. At low column concentration, the triangular columns assemble side-by-side into small clusters via individual plate or column addition (see “hexamer” formation in Fig. 4c), indicating a directional attraction between columns that is strong enough to hold them together once coming close. At high column concentration, the elementary side-by-side attachment extends to 3D honeycomb lattice domains (Fig. 4a, d with inset FFT).

In comparison with the previous hexagonal lattice, the honeycomb lattice domains exhibit high orientational order and positively correlated plate rotation in a nearest neighbor pair of columns. The first-layer plate orientation distributions (by measuring the orientations of the three sides of a plate; Supplementary Note 8) show a six-fold orientational order (bottom right plot in Fig. 4d), consistent with a honeycomb lattice. The two plates in a nearest neighbor column pair have greatly hindered rotations that are positively correlated (a Pearson correlation coefficient of 0.51, Fig. 4f, Supplementary Movie 6), which suggests side-by-side arrangements. Furthermore, upon an ionic strength decrease from 6 to 2 mM in a similarly truncated plate system ($\bar{m} = 0.16$), we observed a transition from the space-filling honeycomb lattice composed of triangular columns to a loosely packed structure which exhibits hexagonal packing due to increased electrostatic repulsion and lowered penalty for relative plate rotation (Supplementary Fig. 15). Such precise control of the final 3D lattice structures arises from the effective shape and consequent coordination symmetry of the column secondary building blocks. Anisometry in the plates drives 3D hierarchical assembly, which proceeds one step at a time and enables engineering of the intermediate product, a strategy molecular crystal engineering adopts to obtain a rich library of crystal structures.

Control experiments on the 2D assembly of silver plates at different plate concentrations did not show ordered structure formation (Supplementary Fig. 16).

Discussion

In our study of anisometric colloidal self-assembly, two otherwise separated length scales merge to induce 3D hierarchical self-assembly. Fundamentally the anisometry encodes highly directional interactions and induces the formation of secondary building blocks, which enable the selection of final structures from polyomorphs over an otherwise complicated free energy landscape. Beyond the conventional small molecular ligands used here, macromolecular shellings or ligands that are responsive to external fields can also be introduced to the anisometric colloids to render patchy interactions or non-equilibrium assemblies, thereby aiding self-assembly into further complicated 3D superstructures. The colloidal shapes as well as the basic quantum-confinement properties can have rich variations. For example, star-shaped or other polygonal basal planes have architecture-dependent plasmonic coupling which can be potentially modulated in the form of 3D arrays as optoelectronic devices. Remarkably, our experimentally observed 3D hierarchical lattices are different from those adopted by simulated triangular prisms, which only form into honeycomb lattices due to hard-core exclusion, yet resembling those simulated for high aspect-ratio circular disks. The combination of positional order and orientational disorder we observed is reminiscent of molecular systems. For example, plate-like molecules can stack into columnar phases to harness longitudinally-favored charge conduction paths and show greater conductivity along the columns than in the perpendicular direction. Molecules such as boron-containing “connectors” or hydrocarbon “linkers” can...
form into covalent organic frameworks, with cage architecture and rotational order developed upon a delicate balance between intermolecular attraction (van der Waals, π–π stacking) and electrostatic repulsion. The formation of covalent organic frameworks is similar to the formation of our honeycomb lattice from triangular plates, upon a balance of interparticle interactions. The real-time dynamics observed here can potentially provide insight into phenomena taking place in those molecular systems.

Methods

Chemicals

Sodium citrate tribasic dihydrate (≥99.0%, HOC(COONa)_3·2H_2O, Sigma-Aldrich), sodium borohydride (99%, NaBH_4, Sigma-Aldrich), silver nitrate (≥99.0%, AgNO_3, Sigma-Aldrich), i-ascorbic acid (≥99.0%; Sigma-Aldrich), citric acid monohydrate (99.0–102.0%, (HO)_3C-C_6H_2(OH)(CO_2H)·H_2O; Fisher Scientific), sodium chloride (99.3%, NaCl; Fisher Scientific), hydrogen peroxide (30 wt %, H_2O_2; Macron), and 2-(2-[2-(1-mercaptoundecyloxy)-ethoxy]-ethoxy-ethoxy-ethoxy-ethoxy-acetic acid (≥99.5%, HS-C_11(OC_2H_4)\_6OCH_2COOH) to improve colloidal stability in solution. Specific Aldrich), silver nitrate (≥99.0%, AgNO_3, Sigma-Aldrich), i-ascorbic acid (≥99.0%; Sigma-Aldrich), citric acid monohydrate (99.0–102.0%, (HO)_3C-C_6H_2(OH)(CO_2H)·H_2O; Fisher Scientific), sodium chloride (99.3%, NaCl; Fisher Scientific), hydrogen peroxide (30 wt %, H_2O_2; Macron), and 2-(2-[2-(1-mercaptoundecyloxy)-ethoxy]-ethoxy-ethoxy-ethoxy-acetic acid (≥99.5%, HS-C_11(OC_2H_4)\_6OCH_2COOH) to improve colloidal stability in solution.

Synthesis of anisometric silver plates

The silver plates of controlled extent of truncation were synthesized following a slightly modified seed-growth method. Silver seeds were prepared by adding 25 mL AgNO_3 (0.1 mM), 600 μL sodium citrate (75 mM), and 60 μL hydrogen peroxide (30 wt %) in sequence to a 125 mL Erlenmeyer flask stirring at 300 r.p.m. at room temperature. Next, the stirring speed was increased to 1050 r.p.m. before rapid injection of 250 μL freshly prepared aqueous NaBH_4 solution (0.1 M). This NaBH_4 solution was prepared by adding solid NaBH_4 to water, which had been precooled in an ice bath for ~10 min and then vortexing immediately. The obtained light yellow solution turned blue after about 4–10 min after the injection of the NaBH_4 solution and was kept stirring for another 5 min after this color change. Then the mixture was centrifuged (Eppendorf Centrifuge 5804) at 10,500 r.p.m. for 8 min and most of the supernatant was carefully removed, leaving ~50 μL sediment. This sediment was dispersed in 10 mL 0.94 mM sodium citrate solution as the seed solution. A UV–Vis spectrum of the as-prepared seeds was measured using a Scino S-4100 PDA spectrophotometer. In another batch of seed preparations, the extinction peak positions were at 480 nm and 520 nm for the 3D- and 2D-crystalline species, respectively. We diluted these solutions using 0.94 mM sodium citrate solution to a concentration with an extinction intensity of 0.012 or 0.0024 at the maximum peak position; this diluted solution was later used as our seed solution stock to grow silver plates.

All the parameters used in silver plate growth (different size and different extent of truncation) are listed in Supplementary Table 1. Below are the synthesis details of the two typical types of plates for which we studied self-assembly behavior. For plates with m = 0.55 (used in Figs. 1 and 2), 0.75 mL of i-ascorbic acid (0.1 M) was added to 20 mL of the seed solution stock kept in a 40 mL glass vial (Fisherbrand, 29 mm × 94 mm) as growth solution I. At the same time, a separate growth solution II was prepared by mixing 20 mL AgNO_3 (0.1 mM), 125 μL citric acid (0.1 M), and 100 μL sodium citrate (1.5 mM). Growth solution II was added to growth solution I dropwise through a syringe pump (Fusion 200, Chemex Inc.) at a rate of 0.2 ml min⁻¹ to start the plate growth. During the growth process, the growth solution was shaken vigorously at room temperature at a stirring speed of 700 r.p.m. for the first cycle and 1000 r.p.m. for the later cycles (Eppendorf ThermoMixer C). After every 10 min of injection, which is one growth cycle, the growth solution was shaken vigorously at a speed of 900 r.p.m. for the first cycle and 800 r.p.m. for the later cycles; (ii) the injection rate of growth solution II was 0.4 mL min⁻¹, with 5 min injection as one growth cycle; and (iii) plates after growth cycle 3 were collected and used for thiol modification.

Thiol modification of silver plates

The silver plates obtained above were coated with citrate ligands. These ligands were exchanged with carboxylate–thiols (HS(CH_2)_n(OH)C_6H_5OCOOH) to improve colloidal stability in solution. Specifically, 100–200 μL 7.93 mM thiol solution was added to 2 mL silver plate solution collected from the growth cycle. This 7.93 mM thiol solution was prepared by diluting 50 mM thiol solution received from Prochimia in 1 mL water. The reaction solution was then allowed to sit overnight without stirring to complete the ligand exchange. After that, the plates with exchanged ligands sediment to a thin layer at the bottom of the vial. The supernatant was carefully removed, and 2 mL water was added to the sediment. After 5 h of additional sedimentation, the supernatant was removed and the final sediment product was stored in water in an 8 mL glass vial.

Plate characterization

The shape and size distribution of silver plates and the assembled 3D lattice structures were characterized using SEM (Hitachi S4800). The plate thickness was measured using either tapping-mode AFM (Asylum Research Cypher) or SEM when the plates were vertical to the viewing angle. The silicon wafer used in the AFM measurement was first sonicated with acetone and isopropanol each for 15 min, and then treated with oxygen plasma (Harrick Plasma Cleaner PDC-23G) at medium power for 1 min to render the wafer surface hydrophilic. Then one drop of silver plate solution (~5 μL) was pipetted on the wafer and allowed to dry under ambient conditions before the AFM measurements. The 3D lattice structures formed in solution in the optical microscopy chamber were controllably dried in the chamber under ambient conditions, to maximally maintain the structure for SEM imaging.

Optical microscopy imaging

Approximately 150 μL silver plate suspension after thiol modification was added to an eight-well chamber (composed of a 0.13–0.17-mm-thick cover slip with plastic walls, Chambered Coverglass, Thermo Scientific). Bright-field optical microscopy imaging was performed using a Zeiss inverted microscope (Axiovert 200) with ×100 oil objective (NA = 1.45) and x1 or x1.6 post magnification. Optical microscopy movies were recorded using a complementary metal-oxide-semiconductor camera (Edmund Optics 5012 M GGE) at a rate of 17.2 or 21.8 frames per second (fps).

SAXS measurements

SAXS measurements were conducted on the truncated plate sample (m = 0.55) to confirm that plates stack face-to-face into columns and to measure the equilibrium plate-to-plate spacing between adjacent plates in the columns at certain ionic strengths. Specifically, the columns were prepared by adding salt to a concentrated plate suspension to an ionic strength that induces self-assembly (0.9 mM). Next, SAXS samples were prepared by gently transferring 100 μL as-prepared columns at the desired ionic strength into a quartz capillary (1.5 mm outer diameter, 0.01 mm wall thickness; Hampton Research), which was then sealed with poly(tetrafluoroethylene) tape to prevent any evaporation. We waited for 3 h for the sample to equilibrate at the bottom of the capillary. Right before the SAXS measurement, the capillary was gently shaken a few times to disperse the concentrated columns uniformly at the bottom of the capillary.

Transmission SAXS spectra were collected for ~10–30 min using a homemade setup (ForvTechs, Santa Barbara) with a Xenon GeniX3D Cu Ka ultralow divergence X-ray source (1.54 Å/8 keV) with a divergence of ~1.3 mmrad and a Pilatus 300 K 20 Hz hybrid pixel detector (Dectris). FIT2D (European Synchrotron Radiation facility, http://www.esrf.eu/computing/scientific/FIT2D) was used to analyze the two-dimensional (2D) scattering plots and obtain the intensity (I) and scattering vector (q) profile (Supplementary Fig. 4). The fact that q values in the SAXS spectra are integer multiples indicates a 1D lamellar structure (see Supplementary Table 3). Due to the large plate-to-plate spacing of the assembled columns, the two first peaks (those with q values <0.01 Å⁻¹) were overwhelmed by the profile of the unscattered beam. Consequently, the q values of the first two peaks were derived from higher-order peaks (Supplementary Table 3). The equilibrium center-to-center distance between neighboring plates in the columns, d, was calculated based on the derived first-order peak position (q_1) as 

$$d = \frac{1}{q_1}$$

where

$$E_{vdW}(d) = \frac{H_{vdW}S}{12} \left(1 - \\frac{2}{d + \frac{\xi}{2}} + \frac{1}{(d + 2\xi)^2}\right)$$

and

$$E_{el}(d) = \frac{\varepsilon \varepsilon_0 k T}{b \left(1 - \tan \theta \left(\frac{d - 2\xi}{2\xi}\right)\right)}$$

Here, \(d\) is the face-to-face spacing between two neighboring plates, \(\varepsilon_{vacuum}\) is the plate thickness, and \(\varepsilon\) is the plate plate basal plane area. In the electrostatic potential, \(\varepsilon\) is the relative permittivity of water, \(\varepsilon_{vacuum}\) is the vacuum permittivity, \(\xi\) is the zeta potential of the thiol-coated silver plates in water, and \(b\) is the Debye length, given (in nanometers) for an aqueous solution of sodium chloride salt as \(b = \frac{8.4}{k T} 10^{-9}\) for ionic strength \(I\) in molar units. In addition, \(\xi_{water}\) is the thickness of the carboxylate–thiol monolayer on the plate surface. Here we assumed that the two plates are in a perfectly aligned, face-to-face configuration.

Because the plates in this system achieve large interparticle separations, the Hamaker constant was treated as an "effective" Hamaker constant in such a way that the retardation of the van der Waals attraction at large separations is
accounted for. In other words,

\[ H_{\text{eff}} = \frac{H_0}{1 + \frac{a^2}{\lambda^2}} \]  

(3)

Here \( a \) is constant describing the geometry of the interaction (\( a = 5.3 \) for two surfaces, \( a = 11 \) for two spheres, and \( a = 14 \) for a sphere and a surface) and \( \lambda \) is a parameter describing the onset length scale for retardation. \( H_0 \) is the Hamaker constant for silver and silver interacting across wafer at zero separation (\( 4.0 \times 10^{-19} \text{ J} \)). This model was previously shown to be a simple but robust approximation for more complicated retardation theories. The value of \( \lambda \) can be approximated by

\[ \lambda = \frac{4c}{\Delta E} \]  

(4)

where \( h \) is Planck’s constant, \( c \) is the speed of light, and \( \Delta E \) is a “characteristic energy” in the electronic spectrum of the material, commonly taken to be the first ionization energy. For silver, \( \lambda \) is therefore about 164 nm.

Net interaction potentials and the locations of their secondary minima at different ionic strength conditions are indicated in Supplementary Fig. 3, as calculated using the values in Supplementary Table 2.

**Discretized modeling of pairwise interactions.** The interaction models discussed above do not account for the relative rotation of the plates perpendicular to the column axis. Therefore, we also constructed a coarse-grained (CG), pairwise interaction model to evaluate the effect of relative plate rotation on the interaction potential (Figs. 3 and 4). Anisometric plates were discretized as \( N = 21,392 \) to 26,744 beads per plate (depending on the extent of truncation) with beads 17.5 nm in diameter (Supplementary Fig. 3a). Beads were treated as point-like particles, whose van der Waals and electrostatic interactions can be approximated by

\[ \psi_{\text{vdW}}^i(j) = -\frac{A_{\text{vdW}}}{r_{\text{vdW}}^6} \]  

and

\[ \psi_{\text{ele}}^i(j) = \frac{Z_i^2 e^2}{4\pi\varepsilon_0 r_{\text{ele}}^{10}} \]  

(6)

where \( r_{\text{vdW}} \) is the distance between beads in a pair, \( r_{\text{ele}} \) is the bead size, and the remaining variables have the same meaning as in the above analytical modeling. The charge of a bead, \( Z_{\text{bead}} \), was approximated first by calculating the surface charge density, \( \rho_{\text{surf}} \), based on the zeta potential, using the Grahame equation:

\[ \rho_{\text{surf}} = \sqrt{8\varepsilon_0\varepsilon RT \sinh \left(\frac{e\zeta}{2k_B T}\right)} \]  

(7)

finding the total charge of the plate surface, and then dividing this charge across all \( N \) beads.

The van der Waals interaction between anisometric plates was taken as the sum of all bead–bead van der Waals interactions, i.e.,

\[ E_{\text{vdW}}(d) = \sum_{i=1}^{N} \sum_{j=1}^{N} \psi_{\text{vdW}}^i(j) \]  

(8)

for beads in one plate and beads in the other. Similarly, the plate–plate electrostatic interaction was evaluated as

\[ E_{\text{ele}}(d) = \sum_{i=1}^{N} \sum_{j=1}^{N} \psi_{\text{ele}}^i(j) \]  

(9)

Note that for the electrostatic interactions, the ligand length was taken into account in determining the interbead distance, depending on whether the beads were on the near, opposite, or same faces of the plates. Net van der Waals and electrostatic interactions were determined in this manner for a series of interparticle distances. The two potentials then were fit in Origin to curves of standard form for interparticle interactions:

\[ E_{\text{vdW}}(d) = \frac{A_{\text{vdW}}}{d^6} \]  

(10)

and

\[ E_{\text{ele}}(d) = A_{\text{ele}} e^{-d/B_1} \]  

(11)

with fitting parameters \( A_1, A_2, B_1, \) and \( B_2 \). The sum of these two curves, \( E_{\text{total}} \), was used to determine the position of the secondary energy minima, using Mathematica. We also evaluated the bead size effect by calculating the van der Waals interaction using a smaller bead size (8.75 nm in diameter) and the results are consistent with different bead sizes (Supplementary Fig. 3b).

To assess the validity of the CG approximation, we first compared the analytical and CG models assuming no rotation between the plate pair. A comparison of interaction curves based on the two calculations at various ionic strengths is given in Supplementary Fig. 3c. Supplementary Figure 3d demonstrates that the relevant features—secondary energy minima and their positions—are predicted with reasonable agreement. We therefore proceeded to use the CG model to determine the interaction of plates with various degrees of rotation and/or truncation.

**Data availability**

All the other remaining data are available within the article and Supplementary Files, or available from the corresponding authors upon request.

**Code availability**

Custom Matlab codes for image processing, particle tracking, and particle interactions are available from the corresponding authors upon request.

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Author contributions
B.L., A.K. and Q.C designed the experiments. B.L., A.K., Z.W. and J.K. performed the experiments. J.W.S. and Z.O. contributed to the theoretical modeling of interparticle interaction. All contributed to writing the manuscript.

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