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Prismatic confinement induces tunable orientation in plasmonic supercrystals

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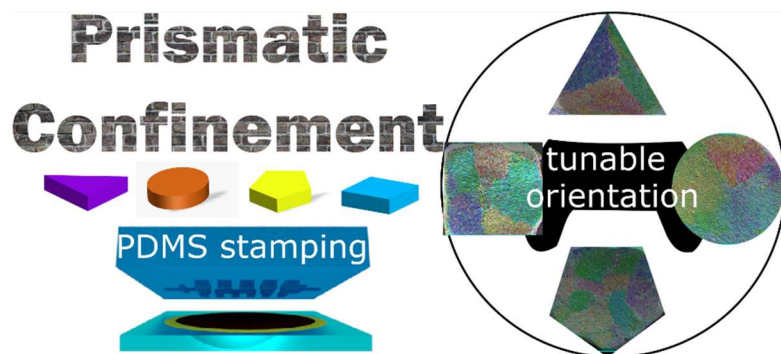
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TOC



Abstract

Throughout history, scientists have looked to Nature for inspiration and attempted to replicate the intricate complex structures formed by self-assembly. In the context of synthetic supercrystals, achieving such complexity remains a challenge due to the highly symmetric nature of most nanoparticles (NPs). Previous works have shown intricate coupling between the self-assembly of NPs and confinement in templates such as emulsion droplets (spherical confinement) or tubes (cylindrical confinement). This study focuses on the interplay between anisotropic NP shape and tunable “prismatic confinement” leading to the self-assembly of supercrystals in cavities featuring polygonal cross-sections. A multiscale characterization strategy is employed to investigate the orientation and structure of the supercrystals, locally and at the ensemble level. Our findings highlight the role of the mold interface in guiding the growth of distinct crystal domains: each side of the mold directs the formation of a monodomain that extends until it encounters another, leading to the creation of grain boundaries. Computer simulations in smaller prismatic cavities were conducted to predict the effect of increased confinement. Comparison between prismatic confinement and cylindrical confinement shows that flat interfaces are key to orient the growth of supercrystals. This work shows a method of inducing orientation in plasmonic supercrystals and controlling their textural defects, thus offering insight into the design of functional metasurfaces and hierarchical structured devices.

KEYWORDS: supercrystal polymorphism; Small angle X-Ray scattering; directed self-assembly; gold nanoparticles; Monte Carlo simulations; self-assembly in confinement.

Nature has long inspired scientists with its ability to synthesize complex inorganic nanostructures by consistently exploiting the self-assembly in confinement of (often complex) building blocks. This level of complexity has not yet been reached synthetically with colloidal crystals, because most nanoparticles (NPs) are highly symmetric objects and because their self-assembly is unconstrained. In order to overcome this limitation, the NPs' shape and environment should be tuned to guide and "frustrate" crystallization.¹⁻³ Aspects of self-assembly in confinement⁴⁻⁸ and shape-directed assembly⁹⁻¹⁵ have been studied separately, and while acting together.¹⁶⁻²³ Intricate structures can be engineered by exploiting the geometrical incompatibility between local ordering and the topology of the confinement geometry, as shown for some NPs and microparticles.^{5, 12} For instance, cellulose nanocrystals,¹⁹ nanoplatelets,²⁴ nanospheres⁶ and nanocubes¹⁶ have been assembled into complex structures within emulsions droplets *via* so-called spherical confinement. Although the confinement could be tuned to some extent by controlling the size of the colloids and the volume fraction in the droplets, Laplace pressure does not allow changing the confinement geometry. In a similar vein, NPs have been ordered in cylindrical confinement but the nature of the templates restricted assembly on a curved interface.²⁵⁻²⁷ Recent studies have pointed out that the topology of orientational defects could be directed with flat interfaces, and shown experimentally with microparticles such as silica rods²⁸ and viruses.²⁹ However, the potential of "prismatic confinement" to assemble anisotropic NPs has not yet been explored.

Noble metal nanoparticles exhibit intriguing optical properties attributed to localized surface plasmon resonances, with frequencies highly dependent on nanoparticle composition, morphology, and the surrounding medium.^{30, 31} The organization of gold NPs into ensembles leads to the emergence of new plasmon resonances unattainable by the individual particles, and the resulting optical properties can be further tuned and even enhanced.³²⁻³⁴ Hybrid top-down/bottom-up strategies can be used for integrating colloids into hierarchically structured devices effectively and at low cost.^{35, 36} Those approaches include a collection of techniques based on contact printing and replica molding with an elastomeric stamp, whose structural features direct the deposition of the colloids onto the template or on a substrate of interest.^{5, 37, 38} Since their initial development, a broad range of colloidal materials have been formed by combining evaporation induced self-assembly (EISA) and templating.^{4, 39-43} Frequently, the template features consist in simple geometries (e.g. cylindrical cavities) and are in the same size range as the building blocks, resulting in the deposition of single NPs or in the formation of small clusters.⁴⁴⁻⁴⁷ Some recent developments includes the formation and study of patterned

plasmonic superlattices for lattice plasmon resonance⁴⁸⁻⁵³ and sensing applications.^{46, 54-59} Some work reported the self-assembly of supercrystals within large cavities,^{55, 60-62} but local ordering and the detailed orientation of NPs in the assembly were not explored, presumably because of the challenges in probing the order at different length scales in the material. Overall, controlling the ordering of anisotropic nanoparticles in confinement by template-assisted assembly holds significance from fundamental interest to the development of future plasmonic metasurfaces. In this context, understanding the impact of the template geometry on the final structure of the supercrystals would be an important advancement.

In this study, we explore how the shape of nanoparticles and a tunable confinement influence the self-assembly of supercrystals. The assembly of the supercrystals is directed by a microtextured template featuring an array of prismatic cavities with varying polygonal cross-section. Conventional small angle X-ray scattering (SAXS) and microbeam SAXS (μ SAXS) are employed for large-scale orientation analysis, while scanning electron microscopy (SEM) provides real-space local structural characterization. Our findings reveal that the mold interfaces direct the growth of multiple crystal domains, demonstrating that the confinement geometry controls both the number and orientations of monodomains.

Results and discussion

Gold nanorods (AuNR) were obtained by seed-mediated growth and were uniform in size and shape (length 55 ± 5 nm, width 18 ± 2 nm, **Figure S1**). Self-assembly was conducted by confining a drop of the AuNR suspension between a substrate (silicon wafer or glass slide) and a polydimethylsiloxane (PDMS) template and letting it dry under ambient conditions (**Figure 1A**). The PDMS templates comprised an array of prismatic cavities with a fixed depth of 2 μ m and various cross-sections (circle, triangle, square, pentagon and hexagon) denoted hereafter by their rotational symmetry, i.e C_∞ , C_3 , C_4 , C_5 , C_6 respectively (**Figure 1B**). For supercrystals we use the same symmetry notation, followed by the SC suffix. After confinement and evaporation induced self-assembly, the template is peeled off to leave on the substrate well-ordered superlattices of prismatic SCs (**Figure 1C**).

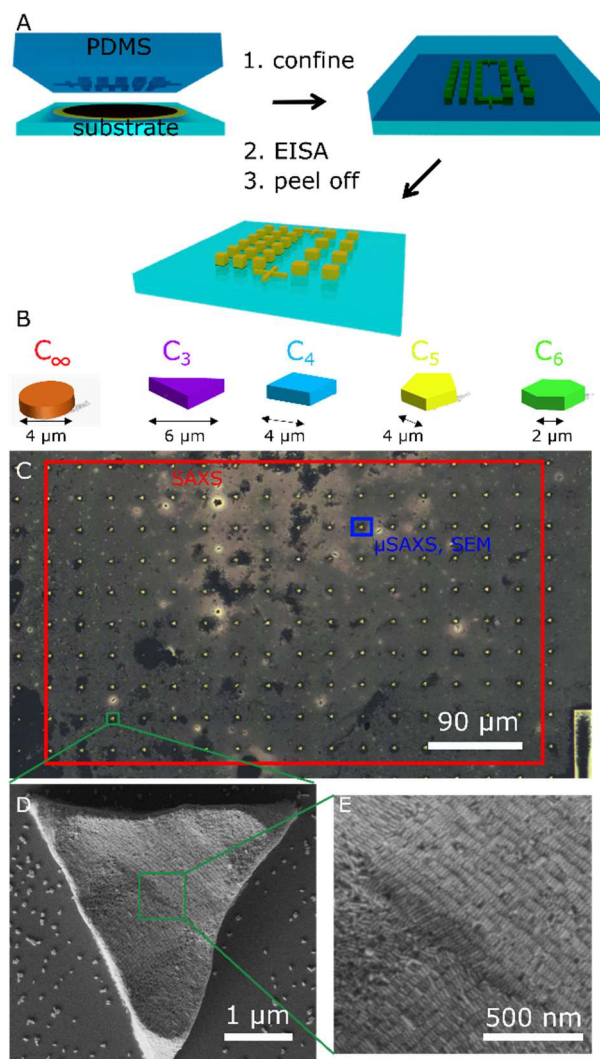


Figure 1: Principle of the method. A) Schematic view of the templated EISA process. B) Schematic description of the shape and size of microcavities, whose cross-sections are denoted by their rotational in-plane symmetry. C) Optical microscopy image of a superlattice of triangular SCs obtained after template-assisted self-assembly and peeling off the PDMS template. The red frame shows the typical footprint of the conventional SAXS beam and the blue one that of the μSAXS beam, which also corresponds to the size of an SEM image. D-E) SEM images of an AuNR triangular SC viewed at different magnifications.

We used a multiscale characterization strategy, as illustrated on **Figure 1C**. Full-beam SAXS was used to characterize the structuration over large length scales, by averaging over hundreds of supercrystals. SEM image analysis revealed the organization of the NPs at the supercrystal surface. Combining high spatial resolution to study individual supercrystals as well as screening the structure of many supercrystals for statistical significance is a technical challenge that cannot be solved either by SEM or by full-beam SAXS.⁶³ In order to achieve this result, a

synchrotron microbeam SAXS (μ SAXS) technique is implemented to study the structuration of many individual supercrystals. In the following, we investigated the structure of the AuNR supercrystals by this multiscale approach, beginning with SEM characterization (**Figure 2**).

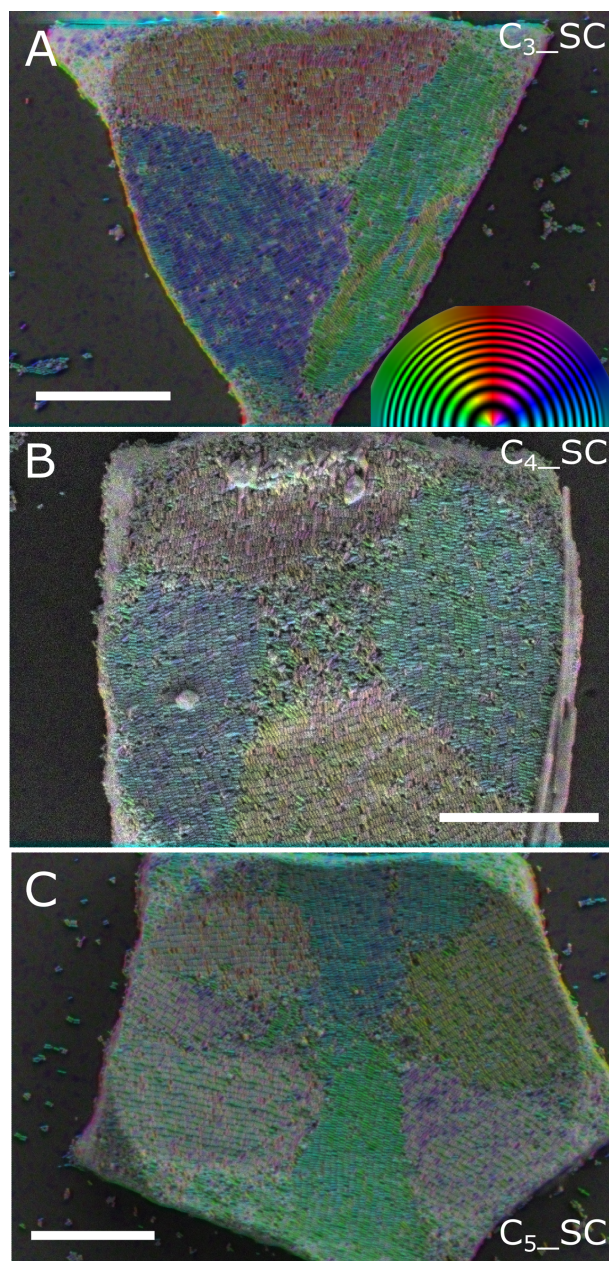


Figure 2: Prismatic supercrystals with templated monodomain orientation. (A-C) SEM images of prismatic SCs with C_3 , C_4 , C_5 symmetry respectively, composed of self-assembled AuNRs. AuNRs are color-encoded according with their orientation for ease of identification of the monodomains. The nanorods' long axis is found to be either perpendicular (C_3 _SC, C_4 _SC) or parallel (C_5 _SC) to the prism facets. Scale bar is $1 \mu\text{m}$ on all images.

In all SEM images, the long axis of most nanorods was parallel to the substrate. SEM image analysis was performed to color-code AuNRs according to their orientation for C₃_SC, C₄_SC and C₅_SC (**Figure 2**). The angular color code is inset in **Figure 2A**. This set of experiments shows that prismatic cavities direct the formation of ordered and oriented monodomains of AuNRs. For instance, three monodomains with orientations evenly spaced by $2\pi/3$ can be observed for C₃_SC. In contrast, four monodomains $\pi/2$ apart were observed for C₄_SC. Similarly, consecutive edges of the C₅_SC generate monodomains related by $2\pi/5$ rotations. However, inspection of many SEM images revealed structural heterogeneities, consisting in varying number of domains and orientational defects (see **Figures S2-S4**). To better understand the templating effect of the prismatic cavities on the distribution of orientational defects at ensemble level, we performed full beam SAXS (**Figure 3**).

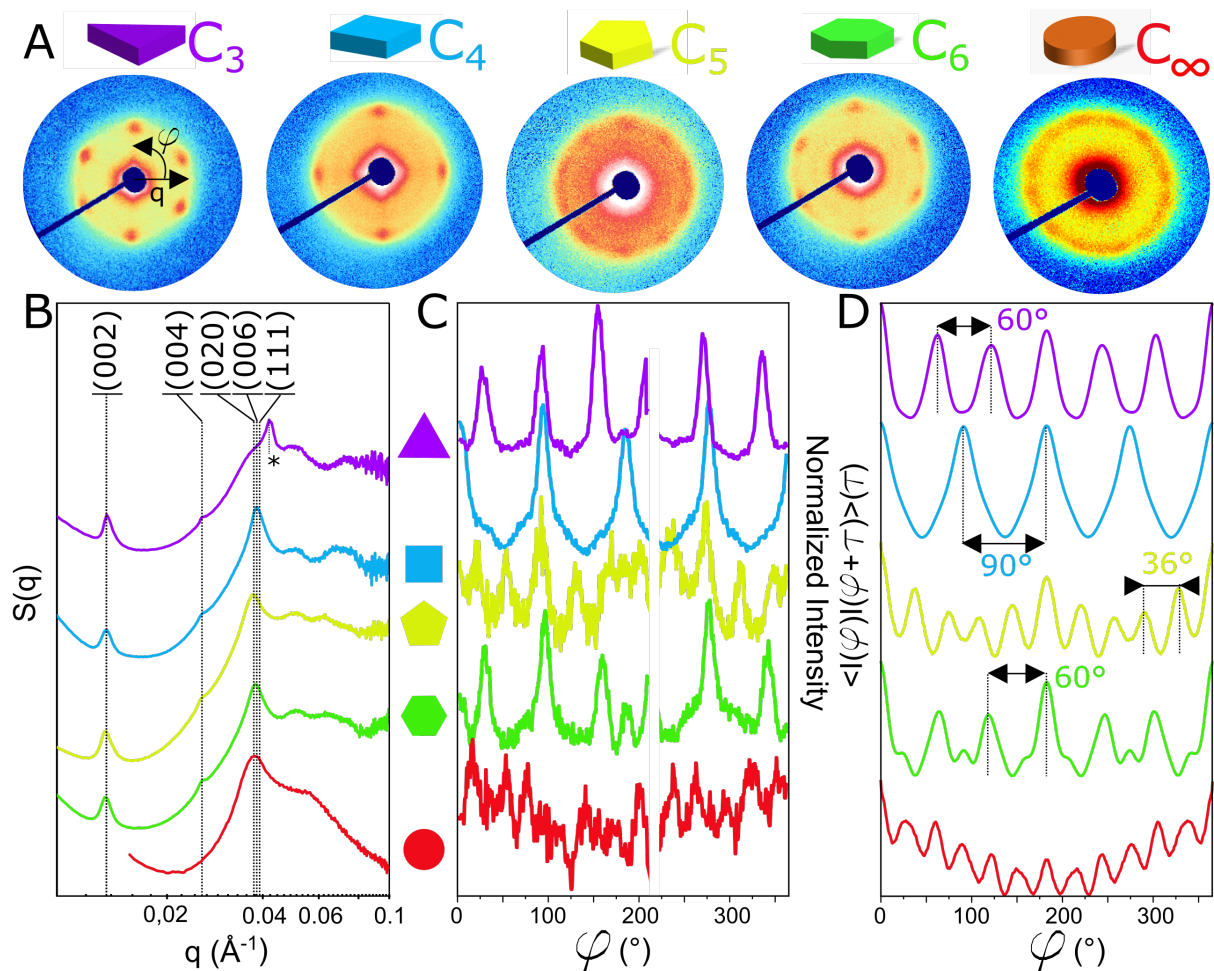


Figure 3: Average structural characterization over hundreds of AuNR supercrystals. A) Two-dimensional SAXS images acquired on different zones of the sample consisting of AuNR supercrystals with different cross-section. The SAXS beam footprint is about $300 \times 300 \mu\text{m}^2$. SAXS images are shown on a logarithmic intensity scale. B) Corresponding structure factors

$S(q)$ of the supercrystals. Vertical lines indicate the expected positions of the Bragg peaks for an orthorhombic crystal. C) Corresponding azimuthal integration $I(\varphi)$ at $q = 0.037 \text{ \AA}^{-1}$. D) Autocorrelation analysis of $I(\varphi)$ to confirm the periodicity of the signals.

On the average, all prismatic supercrystals were highly oriented as shown by discrete Bragg spots on the 2D-SAXS images (**Figure 3A**). In contrast, C_∞ _SC displayed a ring-shaped scattering pattern, indicating the absence of preferential monodomain orientation by cylindrical confinement. Although each measurement consists on averaging the scattering signal of hundreds of SCs, the number of Bragg spots is correlated with the rotational symmetry of the supercrystal: C_3 _SC, C_4 _SC, C_5 _SC, and C_6 _SC exhibited 6, 4, 10 and 6 Bragg spots respectively. Azimuthal integration revealed large differences in crystallographic orientation across the different prismatic supercrystals (**Figure 3C**). *Via* autocorrelation analysis of the SAXS curves (**Figure 3D**), their periodicity was determined to be $\pi/3$, $\pi/4$, $\pi/5$ and $\pi/3$ for C_3 _SC, C_4 _SC, C_5 _SC, and C_6 _SC respectively. In SAXS, each AuNR monodomain gives rise to two equal Bragg spots related by a π rotation, as per Friedel's law. Supercrystals with an odd number of edges, here noted k , such as triangles and pentagons, exhibited $2k$ regularly spaced Bragg spots whereas the ones with an even number of edges, such as squares and hexagons, only displayed k Bragg spots, since in this case two monodomains share an orientation and thus a pair of Bragg peaks. These results imply that each edge of the prism directs the growth of one monodomain (frequently with the rods perpendicular to the interface),^{62, 64} which then grows until encountering another monodomain and forming a grain boundary. In line with this, no adjacent domains shifted by $\pi/2$ were noted for the C_3 _SC, suggesting that the growth starts only from the edges and not epitaxially from the grain boundaries. We conclude that the number of edges of the cavity controls the number and orientation of monodomains in SCs. We next investigated in more detail the structure of the supercrystals (**Figure 4**).

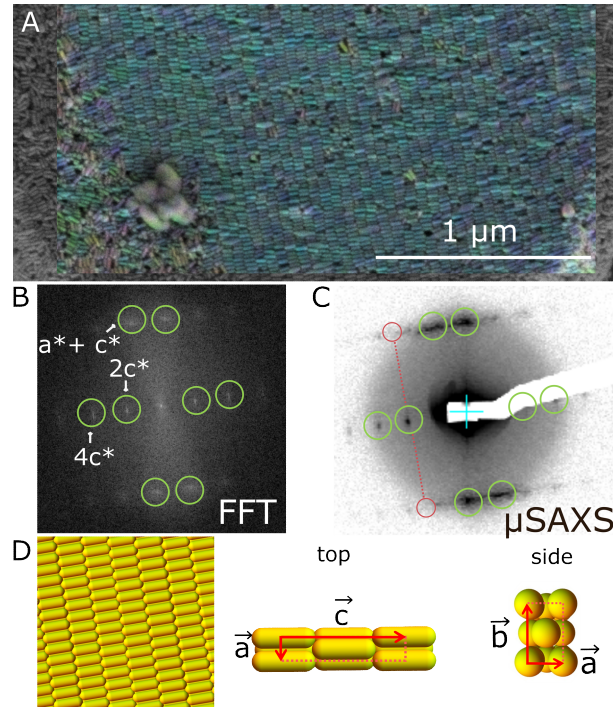


Figure 4: Small-scale characterization of a C_4_SC AuNR supercrystal. A) SEM image of a supercrystal of AuNRs composed of a single monodomain. AuNRs are color-encoded with their orientation. B) Corresponding fast-Fourier transform (FFT) of the SEM image C) μ SAXS image of the same supercrystal (shown on a logarithmic intensity scale). The red circles indicate the expected position of Bragg spots for a hexagonal lattice, which are missing here. The μ SAXS beam footprint is about $20 \times 20 \mu\text{m}^2$. D) Schematic description of the AuNR orthorhombic lattice.

Combined SEM and μ SAXS analysis was performed on a C_4_SC comprising a single monodomain, for ease of analysis (**Figure 4A**). Fast Fourier transforms (FFT) of the SEM images correspond to a 2D image analysis whereas μ SAXS corresponds to a 3D structural characterization. The similarity in the number of spots and their distribution between the FFT and μ SAXS images indicates that the ordering observed on the supercrystal surface is representative of the supercrystal structure in volume (**Figure 4B-C**). This was confirmed on tilted SEM images, where approximately 15 organized layers of AuNRs were observed (**Figure S5**). In 2D, a centered rectangular lattice is evidenced, both in the real and reciprocal space. We initially assumed that the structure of the crystals was hexagonal compact or smectic B, which corresponds to interlayers stacking in a hollow site fashion or to interlayer stacking without registry between the layers respectively, as reported in many works. Instead, we infer the lattice to be orthorhombic from the absence of the a^*+2c^* reflection on the 2D μ SAXS image, in which the expected position is indicated as an open red circle in **Figure 4C**. In comparison with

the hexagonal compact structure, the orthorhombic one corresponds to the intercalation of the hexagonal layers in a bridge site stacking fashion (**Figure 4D**). This last configuration is presumably preferred because all nanorods within the bottom layer are in contact with the substrate.

To bridge the gap between local and macroscale characterization, μ SAXS was performed by scanning the SC lattice and acquiring one μ SAXS image per SC. Azimuthal integration was performed on the 2D μ SAXS images to retrieve the angular distribution of the Bragg peaks. We opted for a representation employing arrows, where relevant information, including the number and orientation of the domains, as well as the extent of order, is encoded through color, direction, and length, respectively (**Figure S6-S7**). The orientation is indicated in the angular range $[0, 2\pi/k]$ and the extent of order is determined from the intensity of the corresponding peak in the correlogram. Amorphous structures are marked by a white dot. The background optical image is acquired in situ during the μ SAXS measurement. Four types of samples are compared using this representation in **Figure 5**: drop-casted SC (no template), C_∞ _SC, C_3 _SC, and C_4 _SC.

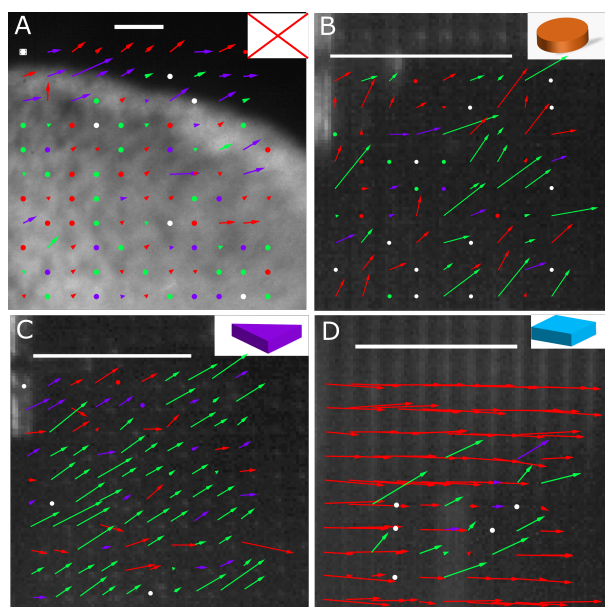


Figure 5: Structural characterization by μ SAXS of AuNR assemblies for varying template geometries. A) no template (drop-casted), B) C_∞ _SC array, C) C_3 _SC array, D) C_4 _SC array. The arrows encode the number and orientation of the domains, as well as the extent of order by their color, direction and length, respectively. C_3 , C_4 and C_5 domains are labeled as green, red and purple respectively. White points mark amorphous structures. The scale bar is 200 μ m on all images.

In the drop-casted sample, the region within the coffee ring exhibited the highest degree of ordering, displaying a preferred orientation compared to the central region (**Figure 5A, Figure S8**). However, the sample demonstrated heterogeneity, featuring small ordered domains of AuNRs, as indicated by the short length, random colors, and directions of the arrows. This μ SAXS result on drop-casted samples aligns with other SEM studies highlighting ordering at the edge of the deposits.^{10, 65} For the C_{∞} _SC the distribution of SCs is more homogeneous across the array but the number of domains and their orientation vary from SC to SC (**Figure 5B**). Although an array of supercrystals is obtained in cylindrical confinement, our results show that prismatic confinement allows better control over the number of domains and their orientation. For instance, the C_3 _SC consisted mainly in three symmetrically oriented domains, confirming the results obtained by full beam SAXS (**Figure 5C**). While the full beam analysis is only sensitive to ensemble ordering, the benefit of μ SAXS is its ability to detect sample heterogeneities, defects and amorphous regions (**Figure S10**). Some SCs with two or five oriented domains and a few amorphous SC were randomly scattered among the C_3 _SC. Similarly, the C_4 _SC are mainly characterized by two orientations across the array, with some occurrence of other nanostructuring (**Figure 5D**). Overall, the multiscale structural characterization of the samples by SEM, SAXS and μ SAXS show that prismatic confinement can be used to control the formation and the orientation of plasmonic supercrystals arrays.

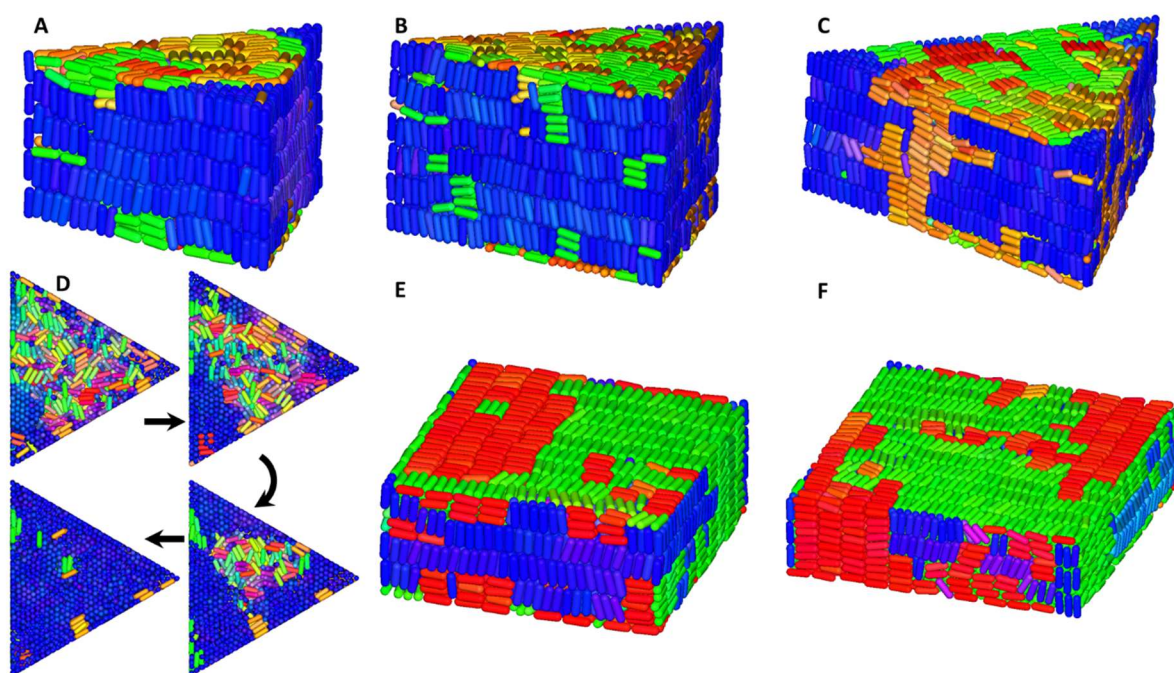


Figure 6: Self-assembly of confined hard spherocylinders in simulations. A-C) Configurations after compression inside triangular geometries with varying edge lengths of the

ground plane ($L_{box} = 10L, 12.5L, 15L$ for A,B,C respectively), and the number of particles chosen to obtain an approximately equally thick final result ($N = 2000, 4000, 5000$, respectively). D) Time development of the internal ordering in a typical system ($L_{box} = 12.5L, N = 4000$), showing a horizontal cut through the box at different times as indicated by the arrows. Note that crystallization starts from the corners. E,F) Same as A-C, but for confinement in a square prism (E: $L_{box} = 10L, N = 4000$, F: $L_{box} = 12.5L, N = 5000$).

In the experiments, our ability to create smaller cavities is restricted by the resolution of photolithography, with minimum size features around $2\ \mu\text{m}$ in edge length, as indicated by the manufacturer. To explore the effects of smaller cavities, we perform computer simulations of hard rods confined in prism-shaped cavities with either a triangular or square ground plane (from $550\ \text{nm}$ to $825\ \text{nm}$ in edge length). In the event-driven molecular dynamics simulations,^{66, 67} the particles start off in a disordered configuration at low packing fraction and are then gradually compressed to high densities by slowly moving down the top confining plate. The systems consist of $N = 1000$ to 5000 spherocylinders with aspect ratio $L/D = 3.17$, where L is the tip-to-tip length and D the rod diameter. Typical results are shown in **Figure 6** for different system sizes. In contrast to the experiments, the rods in the triangular cavities clearly favor vertical alignment, *i.e.* perpendicular to substrate rather than parallel. We attribute this to the fact that in these systems, formation of the smectic layering always starts in the corners of the triangle, where the two vertical walls meeting at an angle of 60° are highly compatible with the structure of a hexagonally ordered layer of vertically aligned rods. This bias is expected to be weaker in larger cavities, where most of the system is far away from the corners of the triangles (which are also less sharply defined), as observed experimentally. In the square cavities, this strong bias is not present, and we observe domains oriented along all three cardinal directions (*i.e.* along the edges of the box), typically resulting in multiple competing domains in the same simulation. Note that **Figure 6** shows results at the packing fraction where the particles are maximally ordered: further compression typically leads to a tilt in the layers of vertically aligned rods, reducing the overall alignment with the walls (**Figure S11**). Our model explores shaping materials by nesting shapes and considers only steric interaction between the walls and the NPs. Although minimalistic, the model accurately reproduce the main experimental observations and thus captures the essential physics behind the phenomenon. Experimentally, PDMS is known to be hydrophobic with a water contact angle of $\approx 110^\circ$,³⁸ thus the NPs suspension was likely not to fully wet the cavities and form a meniscus during assembly. In agreement with this interpretation, the lateral dimension of the supercrystal was smaller than

the one of the cavity (*e.g.* $\approx 3 \mu\text{m}$ for the C_4 _SC dried in cavities with a $4 \mu\text{m}$ square cross section). Other studies pointed out that the shape of the supercrystals can display rounded profiles,^{61, 62} which may be seen as reminiscent of a meniscus formed at the triple contact line between air, the solution, and the substrate. While PDMS has an impact on the shape of the supercrystal, it does not directly affect the local ordering of the nanoparticles because assembly takes place preferentially at the air/water interface rather than the PDMS/water interface.

We next performed the templated assembly of AuBPs (length $66 \pm 4 \text{ nm}$, width $25 \pm 2 \text{ nm}$, **Figure S12** and **Figure 7A**). SEM image analysis reveals the formation of AuBPs supercrystals, characterized by multiple monodomains (**Figure 7B-D**, **Figures S13-S14**). 2D SAXS images were very similar to those obtained with AuNRs in terms of number and distribution of Bragg spots, implying that the microcavity edges also template the growth of oriented AuBPs monodomains (**Figure 7E**). This experiment shows that supercrystals composed of other nanoparticle shapes can also be oriented within prismatic cavities.

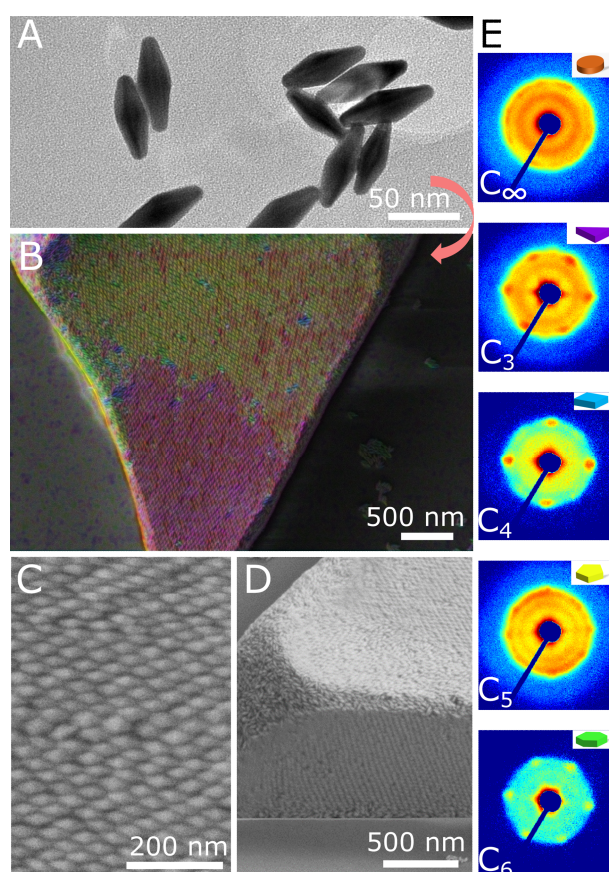


Figure 7: Multiscale characterization of AuBPs prismatic supercrystals. A) Two-dimensional SAXS images acquired at different zones of the sample consisting of supercrystals with different cross-sections. The SAXS beam footprint is about $300 \times 300 \mu\text{m}^2$. SAXS images are shown on a logarithmic intensity scale. B) TEM image of AuBPs. C-E) SEM images viewed

at different magnification and orientation. In C) AuBPs are color encoded with their orientation for ease of identification of the monodomains.

Conclusions

Anisotropic gold nanoparticles were assembled within prismatic cavities by evaporation-induced self-assembly. Using a multiscale characterization methodology, we infer design rules for the formation of prismatic SC with tailored orientation by changing the confinement geometry. Locally, SEM images show the anchoring of gold nanorods to the edges of the cavities, forming SCs with varying numbers of oriented monodomains and a controlled texture. SAXS analysis confirmed the preferred orientation of the monodomains over hundreds of supercrystals. μ SAXS mappings revealed some structural heterogeneity, but overall confirm that this approach provides oriented SCs in high yield. Numerical simulations of hard rods compressed inside a hard prism-shaped confinement show similar domain formation, but display a stronger propensity to align vertically, especially inside triangle-shaped cavities. This difference is likely due to the relatively smaller cavity sizes, perfectly flat walls and sharp corners used in the simulations. The results demonstrate the growth of multiple crystal domains influenced by the mold's interface, where each side directs the growth of a monodomain until it encounters another, resulting in grain boundary formation. Since our approach for orienting supercrystals works for AuNRs and AuBPs, we hypothesize that it can be generalized to NPs superlattices of other relevant shapes such as pentagonal nanoprisms,⁶⁸ platonic solids^{11,69} and nanoplatelets.⁷⁰ Although cylindrical microcavities do not allow controlling the orientation of anisotropic colloids, this work shows that prismatic cavities are promising to orient such nanoparticles on a substrate. In plasmonics, engineering supercrystals with some preferred orientation could be useful for rendering a metasurface sensitive to light polarization, a direction we are currently exploring. Beyond plasmonics, orienting perovskites^{39, 71} or other semiconducting nanocrystals⁷²⁻⁷⁴ within assemblies could lead to amplified and directional emission.

Experimental section

Materials. All chemicals were obtained from Sigma-Aldrich and used without further purification: hexadecyltrimethylammonium bromide (CTAB, $\geq 99\%$), hexadecyltrimethylammonium chloride (CTAC, 25 wt % in H₂O, 90%), hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, $\geq 99.9\%$), silver nitrate (AgNO₃, $\geq 99.0\%$), 5-bromosalicylic acid (5-BrSA, 90%), L-ascorbic acid (AA, $\geq 99\%$), sodium borohydride

(NaBH₄, 99%), trisodium citrate dihydrate (≥99.0%). Water purified by reverse osmosis with a resistivity (>15 MΩ.cm) was used in all experiments.

AuNR Synthesis. AuNRs were synthesized according to previously reported methods.⁷⁵ For the preparation of the seeds, 50 μL of 0.025 M HAuCl₄ solution was added to 4.7 mL of 0.1 M CTAB solution, after mixing, 300 μL of freshly prepared 0.01 M NaBH₄ solution was injected under vigorous stirring. The color of the solution changed from yellow to brownish-yellow and then stirring was stopped after 2 min. The seed solution was aged at 30°C for at least 30 min before injection into the growth solution. The growth solution was prepared by mixing 125 mL of 0.1 M of CTAB with 225 mg of 5-BrSA, 2.38 mL of 0.01 M AgNO₃, 120 mL H₂O and 5 mL of 25 mM HAuCl₄ solution. The process of prereduction was monitored by absorbance spectroscopy, and when the absorbance at 396 nm reached 0.65, 650 μL of 100 mM AA solution was injected quickly under fast stirring. When the solution turned colorless, 400 μL of previously synthesized seed solution was added quickly and the mixture was then kept at 30°C for 4 h. After synthesis, the suspension was purified by 2 rounds of centrifugation (6000 rpm, 40 min) to remove the excess CTAB and then re-dispersed in 2.5 mM CTAC solution.

AuBP Synthesis. AuBPs were synthesized by a seed mediated growth method adapted from the literature.⁷⁶ For the synthesis of the pentatwinned seeds, 33 mL of a 60.6 mM CTAC solution was prepared in a 100 mL Erlenmeyer flask, in which 400 μL of 25 mM HAuCl₄ and 4 mL of 50 mM sodium citrate were added in sequence under gentle stirring. The solution was kept in a water bath at 30°C for 10 minutes. Then, 2.4 mL of freshly prepared 10 mM NaBH₄ solution was injected under vigorous stirring. A reddish solution was obtained after aging the samples during 5 days at 40°C. The seed solution can be stored for at least one month at room temperature. For the synthesis of AuBPs, a 400 mL of 0.1 M CTAB solution was constituted, in which 4 mL of 10 mM AgNO₃, 8 mL of 25 mM HAuCl₄ and 8 mL of 1 M HCl were added in sequence under gentle stirring. Then 3200 μL of 100 mM AA solution was injected under vigorous stirring, followed by the addition of 3200 μL of seed solution when the solution turned colorless. The reaction mixture was left undisturbed at 30°C for 4 h. After synthesis, the particles were purified by at least 3 rounds of centrifugation and pellet redispersion in 2.5 mM CTAC.

Preparation of the PDMS molds. The microtextured mold for the supercrystals was manufactured in PDMS (Sylgard 184, Dow Corning), following standard soft lithography techniques.^{38, 77} The master was purchased from Blackhole lab and was composed of pillars having different shapes and sizes on a 4 inch silicon wafer covered with SU-8 resin. PDMS

(10:1 elastomer to curing agent) was cured at 70 °C for 3 h. In this work, assembly experiments were performed on <100> silicon wafers and glass coverslips.

Preparation of the supercrystals. In all cases, a 10 μ L drop of AuNR or AuBPs dispersion (400 mM in Au⁰ and 2.5 mM CTAC) was deposited on the micro-textured PDMS template and then covered by the substrate. The solvent was subsequently allowed to evaporate to dryness (within 12 h) and the template was then removed, resulting in the formation of arrays of AuNR or AuBPs supercrystals spread over millimeter-sized areas.

UV-Vis-NIR absorbance spectroscopy. The extinction of the gold nanoparticles samples was measured using a Cary 5000 UV-Vis-NIR spectrometer at room temperature, using disposable polystyrene cuvettes with optical paths of 1 cm.

Electronic microscopy: TEM images were obtained on 300 mesh carbon-coated copper grids using a JEOL 1400 microscopy, operating at an acceleration voltage of 120 kV. SEM characterization was performed with a Zeiss Supra55VP with an acceleration voltage of 5 keV.

SAXS experiments. The supercrystal structures were probed by SAXS at the SWING beamline of the SOLEIL synchrotron (Saint-Aubin, France), using a beam energy of 16 keV and a sample-to-detector distance of 6.225 m. μ SAXS was performed with a spot size of 20x20 μ m², 12 keV and a sample-to-detector distance of 6.225 m. Some SAXS data were collected at the LPS using a rotating anode (Cu K α , λ =1.542 Å), and a sample-to-detector distance of 1.396 m. Data treatment (angular averaging and normalization) was done using the Nika 2D SAS macros in Igor Pro.⁷⁸

Simulations. We performed event-driven molecular dynamics simulations^{66, 67} of hard spherocylinders confined by multiple flat hard walls forming either a triangular prism or a square prism. During the simulations, the system is slowly compressed from a dilute disordered phase by lowering the position of the top confining wall with a constant velocity. As this compression heats up the system, a thermostat was used to keep the temperature approximately constant. The simulation is stopped when the pressure in the system becomes so high that the numerical prediction of collisions between particles becomes inaccurate, at which point the system is essentially jammed. The speed of the top plate is set to $10^{-4} D/t$, with D the rod diameter, $\tau = \sqrt{mD^2/k_B T}$ the time unit of the simulation, m the particle mass and $k_B T$ the thermal energy. Faster compression speeds were also explored, and for sufficiently large compression led to more disordered systems with a larger number of domains of aligned particles, as the system has less time to equilibrate during compression. Note that during

compression, the edge length L_{box} of the ground plane of the prism remains constant. Due to the vertical compression, alignment of the particles can often be seen to change non-monotonically with packing fraction as the particles self-assemble into a well-defined number of layers that are forced to tilt as the system is further compressed (see SI).

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Supporting Information Available: TEM images of the gold nanorods and corresponding extinction spectra, SEM images of gold nanorods supercrystals, μ SAXS characterization of the supercrystals, details on simulations, TEM images of the gold bipyramids and corresponding extinction spectra, SEM images of gold bipyramids supercrystals. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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