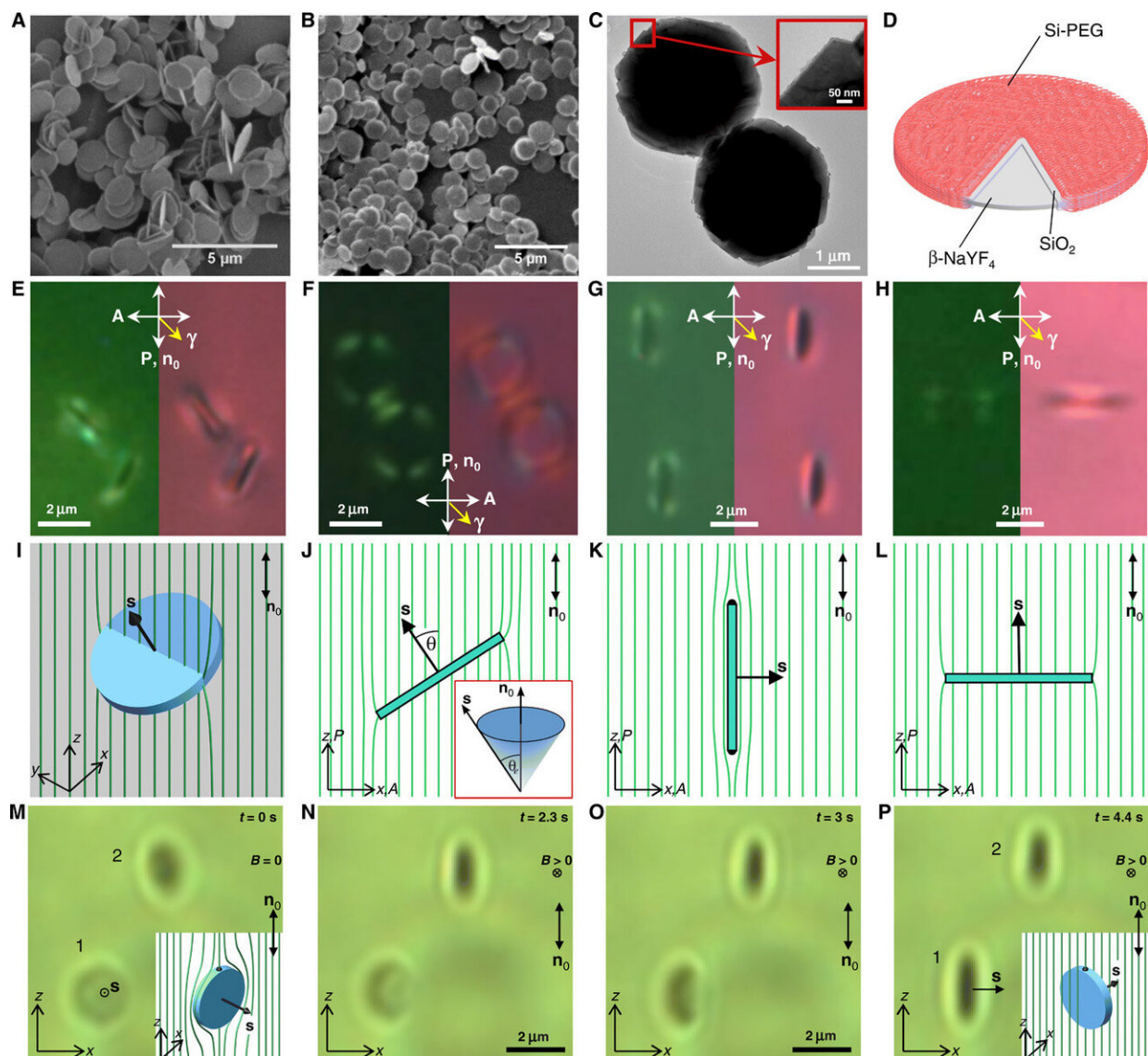


Electrostatically controlled surface boundary conditions in nematic liquid crystals and colloids

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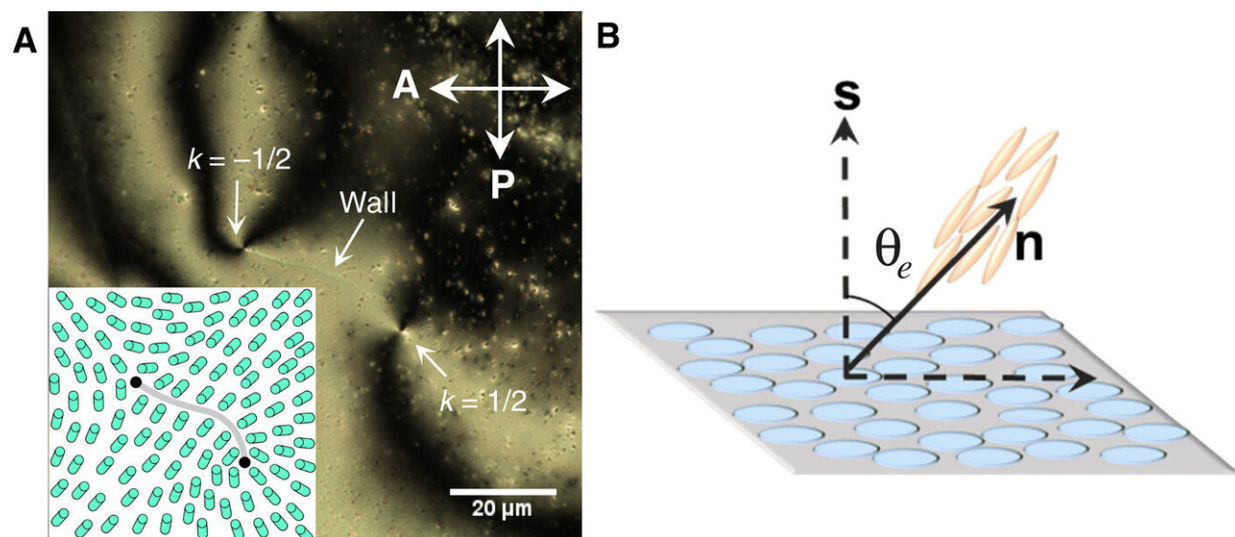
Characterization of the platelets' size and orientation in nematic LC. SEM micrographs of platelets before (A) and after (B) SiO₂ coating. (C) TEM micrograph of particles. The inset shows the SiO₂ layer, visible at the platelet's edge as a thin gray stripe. (D) Schematic of the platelets showing a core, SiO₂ coating, and Si-PEG layer. (E to H) Optical micrographs of platelets with conic (E), planar (F and G), and perpendicular (H) surface anchoring under crossed polarizer P and analyzer A without (left) and with (right) a retardation plate γ in a nematic cell. (I to L) Schematic diagrams of $n(r)$ (green lines) around platelets with conic (I and J), planar (K), and perpendicular (L) anchoring. Inset in (J) is a schematic of conic degenerate boundary conditions. (M to P) Experimental sequence of optical micrographs, with elapsed time marked, showing reorientation of platelets with planar anchoring when a magnetic field $B \approx 480$ G is applied normal to the image planes. Insets show schematics of $n(r)$ around a platelet 1 at $s \perp n_0 \parallel B$ in (M) and $s \perp n_0 \perp B$ in (P). Credit: Science Advances, doi: 10.1126/sciadv.aax4257

Liquid crystals differ from [isotropic fluids](#) (fluids with similar properties in different directions) to exhibit highly [anisotropic](#) (varying properties in different directions) interactions with surfaces. In a new report on *Science Advances*, Haridas Mundoor and an interdisciplinary research team in the departments of physics and soft materials research, electrical, computer and energy engineering in the U.S., controlled the surface alignment of [nematic molecules](#) (strong scatterers of light due to thermal fluctuations within liquid crystals). By controlling the ionic content, the scientists tuned the orientations of the shape-anisotropic, platelet-like particles. The resulting anisotropic, elastic and electrostatic interactions facilitated colloidal crystals with reconfigurable symmetries and orientations. They harnessed the competing aligning effects of surface functionalization and the electric field that arose due to experimental surface charging and bulk [counterions](#) within the setup.

Liquid crystals (LCs) have found applications from [light displays to](#)

[biomedical sensors](#), due to their [anisotropic surface interactions](#). Such surface interactions can define boundary conditions for molecules on particle surfaces, allowing scientists to ultimately determine the [defects and interactions induced](#) during fundamental studies of LC colloids. For [shape-anisotropic particles](#), colloidal assemblies and phases that strongly depend on these boundary conditions varied from [planar](#) to [tilted](#) and [perpendicular](#) orientations. To determine surface orientations in the LC's director field, scientists generally use the anisotropic part of surface free energy, known as the 'anchoring energy.' For a given LC, researchers can control the anchoring energy using [chemical or topographic](#) modifications, [mechanical rubbing](#) or [photoalignment techniques](#). Limited control on surface anchoring can hinder the use of LCs in colloidal assembly and technical applications.

In the present work, Mundoor et al. reported the influence of ions on surface anchoring properties and defined the behavior of anisotropic colloids dispersed in a nematic liquid crystal. The scientists controlled the ionic content in the LC to demonstrate a systematic variation of boundary conditions. They then showed how equilibrium orientations of charged colloidal particles altered relative to the far-field direction and demonstrated the ensuing self-assembly of colloidal arrays with diverse crystallographic symmetries.

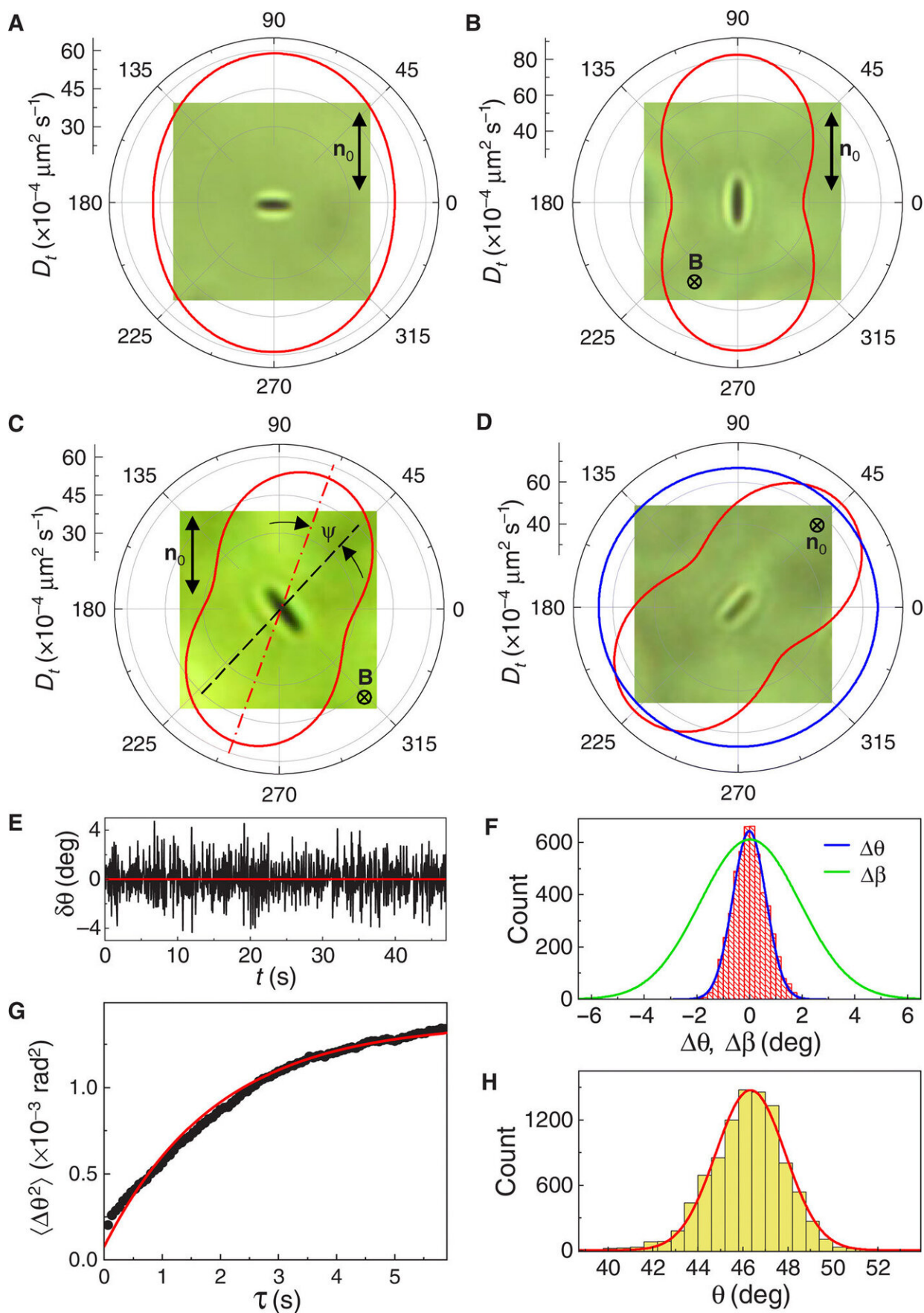


Measurement of tilt angle. (A) Texture of a nematic LC cell with substrates covered with platelets, with conic surface anchoring caused by surface charging; the inset shows $n(r)$ around half-integer disclinations connected by a surface wall defect, indicative of conic boundary conditions. (B) Corresponding schematic of LC alignment with director tilted to the surface normal s . Credit: Science Advances, doi: 10.1126/sciadv.aax4257

The research team synthesized platelet-shaped [β-NaYF₄:Yb/Er microcrystals](#) using a modified [hydrothermal method](#). They optimized the chemical synthesis to yield circular platelets with an average diameter of 2 μm and a thickness of 20 nm, which they confirmed using [scanning electron microscopy](#) (SEM). When the scientists excited the platelets using a 980 nm infrared laser, the particles showed [luminescence upconversion](#). The scientists then chemically treated the particles for [surface charging](#), coated with 5 nm thick silica and functionalized [with methoxy silane polyethylene glycol](#).

The team dispersed the silica-capped particles in [4-cyano-4'-pentylbiphenyl](#) (5 CB) [liquid crystal](#) by mixing it with a dilute

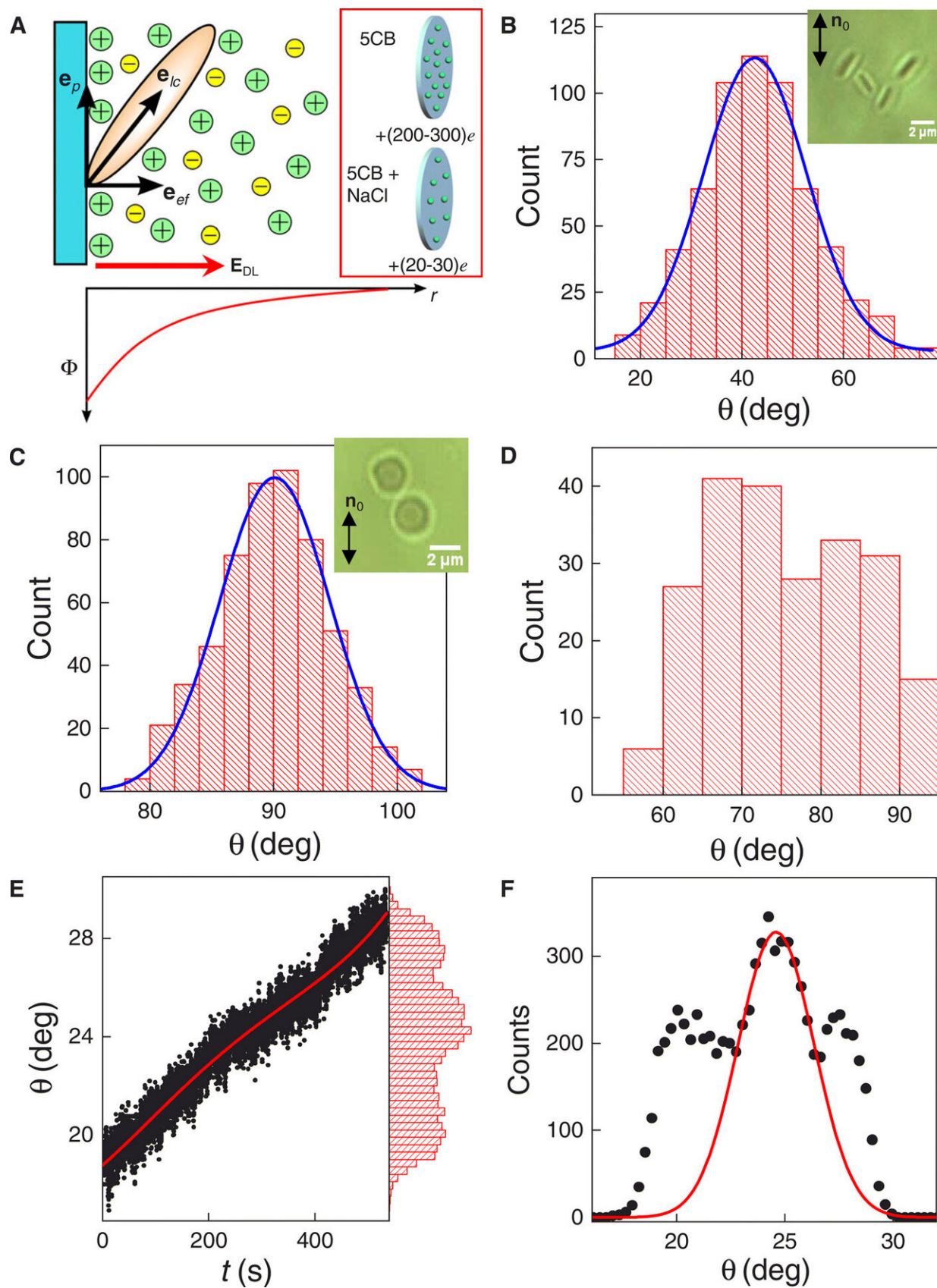
colloidal dispersion in ethanol, followed by solvent evaporation at 70° C for 2 hours. They then cooled down the particles to the nematic phase under rapid mechanical agitation. Munderoor et al. infiltrated the ensuing colloidal dispersions into 30 μm -thick glass cells and sealed them with a fast-setting epoxy glue. They promoted the planar boundary conditions by coating the inner surfaces of the glass cells with polyvinyl alcohol, followed by studying the dispersion and alignment of particles within the LC using optical microscopy. They studied the polarizing optical micrographs to reveal configurations of the particles at different orientations as well as the response of platelets to electric and magnetic fields in LC and isotropic media.



Characterization of translational and rotational diffusion of platelets.

Translational (A to D) and rotational (E to G) diffusion of platelets in a nematic LC. (A to C) Dt of a platelet with (A) perpendicular, (B) planar, and (C) conical boundary conditions in a planar cell with in-plane n_0 ; black and red dashed lines in (C) show a normal to the platelet and a direction of maximum displacements, respectively. Magnetic field $B \approx 480$ G in (B) and (C) keeps the orientation platelet's s parallel to the field of view. (D) Dt of a platelet with planar surface anchoring in a homeotropic cell; red and blue plots show Dt with respect to the cell and particle coordinate frames, respectively. Inset micrographs in (A) to (D) show the actual platelets undergoing diffusion. (E) Orientational fluctuations $\delta\theta$ of a tilted platelet in (C) with respect to its preferred orientation θ_e versus time t obtained at $\tau = 67$ ms. (F) Histograms of angular displacements $\Delta\theta$ and $\Delta\beta$ obtained at $\tau = 67$ ms, respectively, in planar and homeotropic cells. The solid blue and green lines are Gaussian fits. (G) Angular mean square displacement $\langle\Delta\theta^2\rangle$ versus lag time τ in a planar cell. A solid red line is a fit of experimental data (black filled circles) with $\langle\Delta\theta^2(\tau)\rangle$. (H) Histogram of platelet orientations obtained at $\tau = 67$ ms during ~ 10 min. Credit: Science Advances, doi: 10.1126/sciadv.aax4257

The researchers then formed an experimental cell using two glass substrates with dense layers of platelet spin-coated to their inner surfaces. Using the experimental setup, they measured the optical phase retardation of these cells to reveal a 49-degree tilt relative to substrates, which the team could further control via ion doping within the system. The researchers electrostatically controlled the boundary conditions on confining cell surfaces by coating them with platelets or by using substrate materials with tunable surface charging.

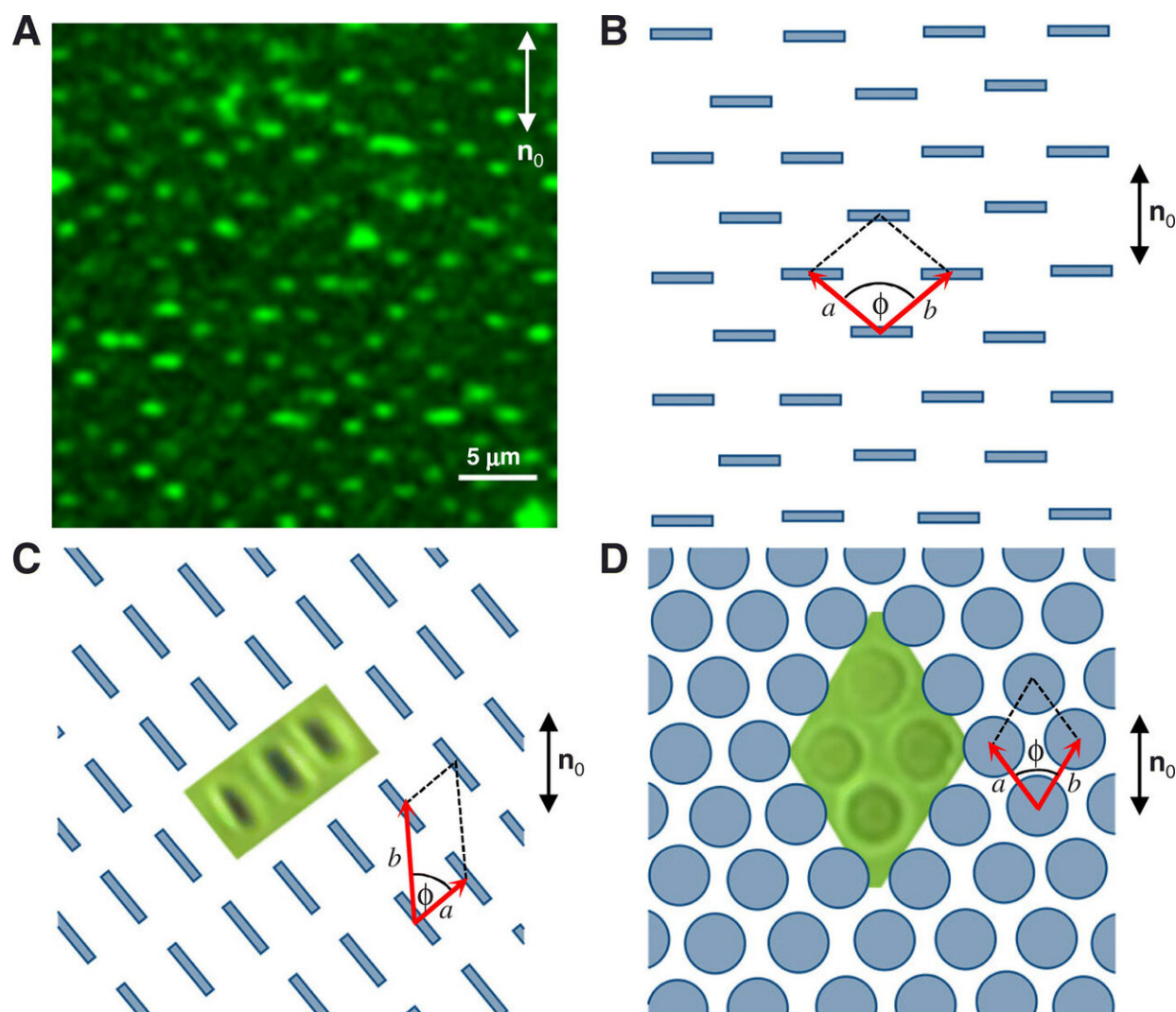


Effect of ionic content of LC medium. (A) Schematic diagram of the LC alignment (an ellipsoid) at the surface (blue); e_p , e_{ef} , and e_{lc} show the easy axes determined by interactions with the polymer capping, electrostatic interactions, and the LC alignment resulting from their competition, respectively. Φ is an electric potential varying over the thickness of the double layer, and r is a distance from the platelet surface. A red arrow shows the direction of EDL. Positive and negative charges are shown by green and yellow filled circles, respectively. The right-side insets schematically show the density of a positive charge (green spheres) at the platelet surface in as-purchased and doped 5CB. (B to D) Distributions of orientation for platelets in a planar cell when dispersed in pure 5CB (B) and salt-doped 5CB for NaCl concentrations of 1 nmol/ml (C) and 0.1 nmol/ml (D). Insets in (B) and (C) are optical micrographs of platelets at orientation, tilted and parallel to n_0 in the respective LC media. (E) Change of θ with time for a platelet in pure 5CB due to absorption of ions from the atmosphere. (F) Distributions of platelet orientations showing discrete increments in the angle θ . The red line is a Gaussian fit of the central part of a distribution shown in (E) corresponding to the completed step during the change of the orientation. Credit: Science Advances, doi: 10.1126/sciadv.aax4257

Particle diffusion in the system depended on the interplay of LC's anisotropic viscoelastic properties and the [shape anisotropy of the oriented particles](#). For instance, the platelets with perpendicular or planar boundary conditions distorted the LC's director to form elastic quadrupoles embedded in a uniform background. The research team used [video microscopy tracking](#) of the platelet's position to determine diffusion coefficients. The researchers observed stronger diffusion anisotropy for particles with perpendicular anchoring, where shape anisotropy influenced the diffusion of particles.

Doping with ionic additions such as NaCl caused counterions (that maintain electric neutrality) to adsorb on the particle surfaces, which effectively reduced the surface charge and strength of the [electric field](#)

(E_{DL}). Upon doping, the platelets also reoriented step-wise with time from their original alignment due to changing surface charges. For instance, the platelets gradually re-shaped from discrete orientations for several hundred seconds, before jumping to the next orientation. The detailed mechanism of counterion adsorption during the process remains to be understood and further explained via additional studies.



Self-assembled colloidal lattice formed by platelets. (A) Upconversion luminescence confocal image and (B) schematic of a self-assembled colloidal lattice of charged platelets with perpendicular anchoring in a planar cell. The

measured (defined on schematics) parameters of the rhombic lattice: $a = b \approx 3 \mu\text{m}$, $\phi \approx 100^\circ$. (C and D) Schematics of 2D assemblies in a nematic LC for platelets with tilted (C) and planar (D) boundary conditions. Insets in (C) and (D) show the experimental fragments of corresponding assemblies, where $\theta_e \approx 34^\circ$, $a \approx 2.1 \mu\text{m}$, $b \approx 3.7 \mu\text{m}$, and $\phi \approx 56^\circ$ in (C) and $\theta_e \approx 0^\circ$, $a = b \approx 2.5 \mu\text{m}$, and $\phi \approx 68^\circ$ in (D). Credit: Science Advances, doi: 10.1126/sciadv.aax4257

Mundoor et al. observed that the platelets formed crystalline assemblies at high concentrations due to competing [elastic and inelastic interactions](#). The results showed potential to design [colloidal crystals](#) with crystallography tunable by ion doping, where the addition of salt altered the self-assembly. Platelets with high charge (+300e) showed [homeotropic](#) anchoring and formed a rhombic lattice. When the charge decreased to +100e, they adopted ionic anchoring and tilt to assemble into an oblique lattice with different parameters. When the platelets with the lowest +20e charge and planar anchoring aligned perpendicular to the cell substrates they formed a rhombic lattice. Mundoor et al. could magnetically and electrically reconfigure the two-dimensional (2-D) lattices within the crystallographic planes parallel to the cell substrates to yield diverse 3-D crystals. Such 3-D crystals can be further aligned by tuning [platelet](#) orientations and by electrostatically varying the space between the crystallographic planes in future work.

In this way, Haridas Mundoor and co-workers controlled the anchoring free energy and [boundary conditions](#) on colloidal particles and the confining surfaces of liquid crystals (LCs) by tuning surface charges and by changing the ionic dopant concentration. The work enabled them to control the LC alignment with respect to confining surfaces and control the orientation of anisotropic colloidal particles such as platelets, with respect to the uniform far-field background. The researchers aim to conduct further studies on how topological defects on particle surfaces

and in the LC bulk, could mediate the absorption of counterions. They will also investigate how inhomogeneous electrostatic double layers could be generated from the anisotropic nature of LCs in future work.

More information: Haridas Mundoor et al. Electrostatically controlled surface boundary conditions in nematic liquid crystals and colloids, *Science Advances* (2019). DOI: [10.1126/sciadv.aax4257](https://doi.org/10.1126/sciadv.aax4257)

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