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Device-scale perpendicular alignment of colloidal nanorods

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The self-assembly of nanocrystals enables new classes of materials whose properties are controlled by the periodicities of the assembly, as well as by the size, shape and composition of the nanocrystals. While self-assembly of spherical nanoparticles has advanced significantly in the last decade, assembly of rod-shaped nanocrystals has seen limited progress due to the requirement of orientational order. Here, the parameters critically relevant to self-assembly are systematically quantified using a combination of diffraction and theoretical modeling; these highlight the importance of kinetics on orientational order. Through drying-mediated self-assembly we achieve unprecedented control over orientational order (up to 96% vertically oriented rods on 1cm² areas) on a wide range of substrates (ITO, PEDOT:PSS, Si₃N₄). This opens new avenues for nanocrystal-based devices competitive with thin film devices, as problems of granularity can be tackled through crystallographic orientational control over macroscopic areas.

Colloidal nanocrystals offer a potential route to realizing low-cost solution-processed electronic devices. In particular, with their size-tunable properties, single-crystallinity, and inexpensive synthesis, semiconductor nanoparticles could enable improved optoelectronic devices. To date, however, the performance of nanoparticle devices has been limited, in large part, by the number of interfaces charge carriers encounter before collection is complete; each interface presents an opportunity for recombination and subsequent charge loss or relaxation.

An ideal film would appear as a single-crystal to charge carriers, but would maintain solution-processability and therefore low manufacturing cost. This has been attempted with nanowire arrays¹⁻³, which can have single-crystal properties in the through-film direction (necessary for optoelectronics), but such arrays have met with only partial device success due to the low nanowire packing density and difficulty of incorporating semiconductor material between wires. Using colloidal nanocrystals, researchers have explored carrier mobility and device performance in the context of low-resistivity percolation networks. Improving the percolation network (low-resistivity pathway for charge carriers) has steadily improved performance as devices have evolved from using spheres to randomly-oriented rods to hyperbranched particles^{4,5}. An ideal device geometry would consist of a monolayer of vertically oriented rods (perpendicular to substrate) spanning the full thickness of the film. While vertical nanowires have been formed on substrates using batch processing⁶⁻⁹, the aim of this work was to achieve a perpendicular morphology in one step using solution-processable nanocrystals with no pre-patterning requirements or substrate restrictions.

Several reports of perpendicular alignment of nanorods exist on a small scale ($\mu\text{m}^2\text{s}$)¹⁰⁻¹⁶, but larger areas necessary for devices have not been reported quantitatively, nor is there a firm understanding of the underlying physical principles directly self-assembly, which would allow rational design. A key component missing from the literature until recently is large-scale quantification of nanorod orientation¹⁷. Here, we report a slow-drying method for self-assembly of colloidal nanorods resulting in device-scale perpendicular alignment of semiconductor nanorods. We explore the self-assembly parameter space, and discuss the important role kinetics plays in alignment. This assembly method is general to a variety of substrates and can be expanded to the square centimeter scale.

In this work, nanorod films were produced with both short- and long-range order by controlling the evaporation of a cadmium sulfide nanorod solution (Figure 1). CdS nanorods (4nm in diameter, tunable 30-100nm in length, with octadecylphosphonic acid ligands) were used in these studies due to the well-established synthesis¹⁸ of single-crystal samples monodisperse in size and shape. Before alignment, rods were stored air-free, and rod concentrations were measured with UV-vis absorption calibrated with inductively coupled plasma mass spectrometry. With a slow evaporation rate (<1mm/min meniscus speed across substrate), an elevated

temperature (55°C), and an appropriate substrate (for example, silicon nitride), nanorods oriented vertically. (See Supporting Information for further details.) To better understand the key parameters controlling self-assembly and thus aid rational device design, electron microscopy images were paired with a diffraction measurement technique representative of full-film morphology.

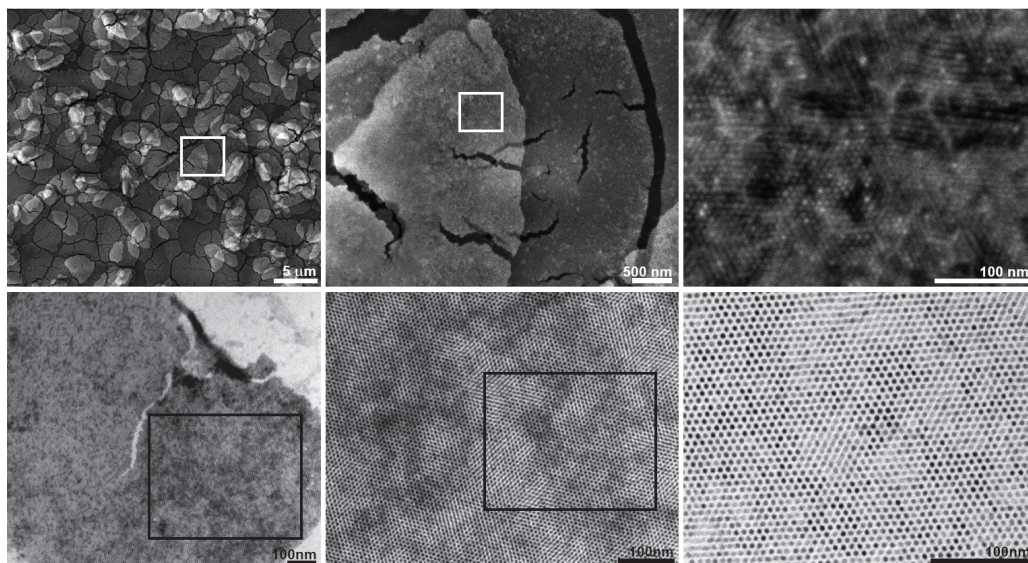


Figure 1. Electron microscopy images of large vertically oriented rod domains with progressive zoom from left to right. Top/bottom row: SEM/TEM images. Regions of higher contrast correspond to multiple monolayers. At this scale, assembly is difficult to judge quantitatively with electron microscopy.

Assembly of quantum *dots* can be assessed with a small-angle x-ray diffraction measurement (which probes the particle-to-particle periodicity, rather than atomic periodicity in individual nanoparticles) because particle rotational orientation is unimportant; only positional information is needed¹⁹. For information about nanocrystal crystallographic orientation, and for easier data interpretation, wide-angle diffraction is more appropriate.

Grazing-incidence wide-angle x-ray diffraction (GIXD) enables morphological quantification of assembled nanoparticle thin-films by leveraging the anisotropic lattice common to many semiconductor nanocrystals (Figure 2). Here, in the case of cadmium sulfide (wurtzite lattice), the long axis of the nanorod corresponds to the c-axis ((002) direction) in the rod's lattice. Therefore, knowledge of the *lattice* orientation translates to knowledge of the *rod* orientation. While any diffraction peak could be used to monitor rod orientation, (002)

was chosen because of the sharp signal afforded by its orientation along the long axis of the rod. (002) diffraction from rods oriented parallel to the substrate falls at the horizon of the Bragg ring in the diffraction pattern (Figure 2 c and d) and corresponds to rod orientation angle $\omega = \pm 90^\circ$. Diffraction from rods oriented perpendicular to the substrate falls at the top of the Bragg ring, where ω approaches 0° . Radial cross-sections of the diffraction pattern taken at different angles show the degree of anisotropy in nanorod orientation (Figure 2e and f). Integrating diffraction intensity as a function of angle ω along the circumference of the (002) Bragg ring gives us an orientation distribution function (Figure 2g and h).²⁰

By using a large X-ray beam size and rastering the beam across the substrate, we obtain an orientation distribution function (ODF) representative of the entire film. By integrating the normalized and intensity-corrected ODF²¹ within a range of angles of interest, one can say with precision how many rods are oriented within this range. Here, vertical is considered to be $\pm 20^\circ$, as this amount of tilt corresponds to a small change in film thickness of only 6%.

Strong texture is observed (intensity variation around Bragg ring) in the diffraction patterns from films of vertically oriented nanorods (Figure 2d), corresponding to a narrow ODF indicating vertical nanorod alignment. The width of the orientation peaks may be due to contraction of the ligand shell upon final solvent drying, causing rods to lean slightly. This could be understood as a cumulative effect of the shrinkage of ligands on many rods (approximately 0.4nm per rod), creating (over the area of tens of rods) enough space for either cracks or rod inclination (see cracks and tilting rods in Figures 1 and S3, respectively).

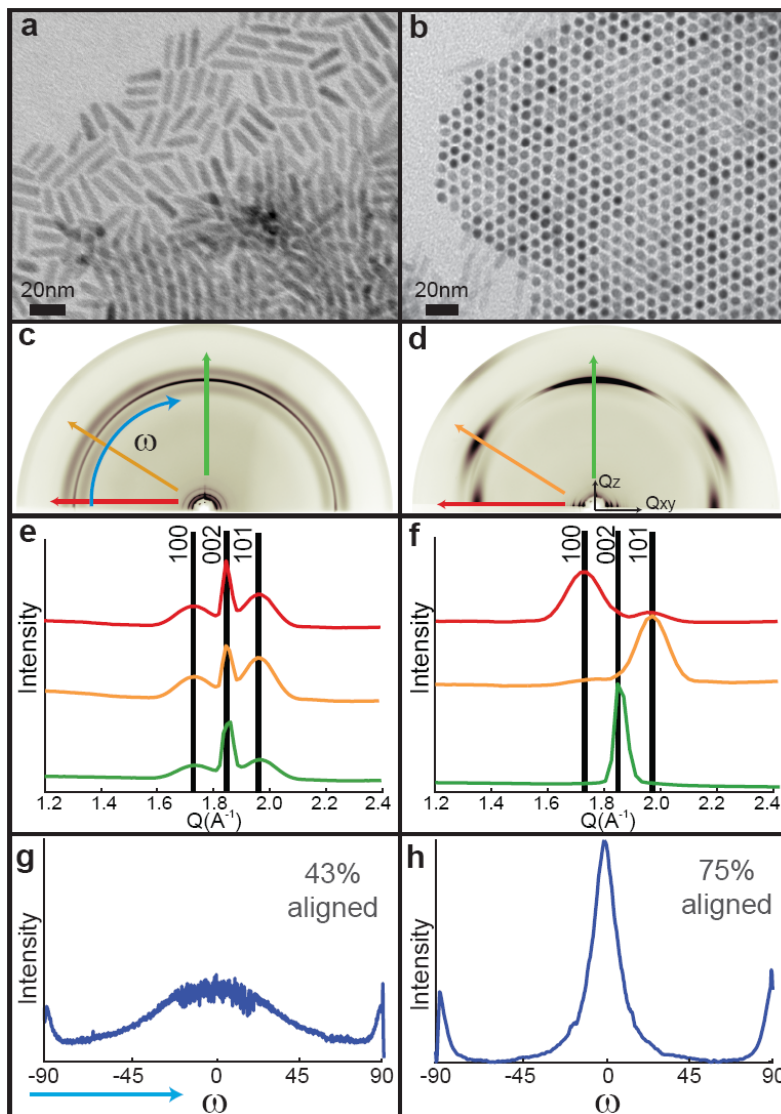


Figure 2. X-ray diffraction is a necessary complement to electron microscopy for film morphology assessment.

(a) and (b) TEM images of near-isotropic and vertically aligned nanorods. The c-axis of the anisotropic wurtzite lattice is oriented along the long axis of nanorods, enabling detection of rod orientation with wide-angle diffraction. (c) and (d) Diffraction patterns corresponding to morphologies (a) and (b). Intensity collected near the horizon of the (002) (middle) Bragg ring is diffraction from horizontally oriented rods, while intensity near the top is from vertically oriented rods. Low-Q intensity is from small-angle diffraction events (superlattice). (e) and (f) Radial cross-sections of diffraction patterns shown in (c) and (d) indicate an angle dependence only in the case of an oriented film. (g) and (h) Orientation distribution obtained by plotting the intensity of rocking and grazing data along the (002) Bragg rings in (c) and (d) as a function of ω ^{21,22}. From these plots, we can determine the percentage of rods vertically oriented (within $\pm 20^\circ$ of the normal to substrate): 43% and 75% are

vertically aligned in (g) and (h). The tails around $\omega=\pm 90^\circ$ in Figure 2h indicate that some of the rods lie horizontally.

To quantitatively explore the dependence of rod alignment on key assembly parameters (temperature, aspect ratio, and van der Waals (vdW) interaction with the substrate (Figure 3)), we used the GIXD analysis described in Figure 2 together with theoretical calculations of interaction energies and diffusion constants. Elucidation of the contributions from entropy, enthalpy, and kinetics gave us insight into the physics governing rod self-assembly. The standard experimental conditions for data plotted in Figure 3 were: 55° C nanocrystal solution temperature, rod aspect ratio 6.4, rod diameter 4nm, polydispersity $\sigma=12\%$, tetrachloroethylene as solvent, Si_3N_4 substrates, and evaporation rates resulting in $\sim 1\text{mm/min}$ meniscus speeds across the substrate. Total number of nanorods in solution was chosen to provide at least one full monolayer of vertically aligned rods on the final substrate. To avoid aggregation, experiments were performed in the presence of excess surfactant (see Supporting Material for nanocrystal cleaning details).

Heating the nanorod solution 10-40°C above room temperature (while keeping evaporation rate constant) favored perpendicular rod alignment (Figure 3a), consistent with previous qualitative reports^{10,14}. This may point to a competition between kinetic, entropic, and energetic effects. The rotational and translational diffusion constants (D^i) for rod-shaped particles²³ depend on temperature as $D^i \propto T/\eta_s$, where η_s is the shear viscosity. Since η_s decreases upon heating, self-assembly will become faster at higher temperature, effectively giving the system more time to lower its free energy. In this case, the increase in alignment upon heating would indicate that the perpendicularly aligned state is thermodynamically stable. The trend in Figure 3a could also indicate that there are entropic effects driving perpendicular alignment. It is well known that hard rod-shaped particles will spontaneously undergo orientational ordering when their containing volume shrinks (due to solvent evaporation) because the gain in positional entropy on alignment more than compensates for the loss in rotational entropy²⁴. Li *et al.* observed similar liquid-crystalline behavior for CdSe nanorods²⁵, which have analogous physical properties to the CdS nanorods used in the present study. In Li's work, the isotropic-nematic phase boundary was found to be weakly temperature dependent over the range considered (these data are

plotted in Figure 3a for comparison). However, in the absence of additional interactions hard rods will align parallel to a hard surface when their containing volume shrinks²⁶, so entropy alone cannot stabilize perpendicular alignment.

Similar to previous reports, we found that low aspect ratio (AR) rods aligned more readily than rods with high AR (Figure 3b). While we were able to align rods with ARs up to 15 (higher than any published report), we were unable to identify a set of parameters that achieved detectable vertical orientation with nanorods of AR approaching 25. This is likely a predominantly kinetic effect. The short-time (non-interacting) rotational diffusion constant D^{rot} for rod-shaped particles in solution is strongly dependent upon their length L ²³. For the size nanorods considered here $D^{\text{rot}} \propto \ln(L)/L^3$, and a reduction of ~97% going from an AR of 5 to 25. The trend for long-time (considering rod-rod interactions) rotational diffusion constants follows a similar trend (see Supporting Material). Based on thermodynamic considerations alone, one would expect the reverse trend: greater alignment with increasing AR. As the AR of hard rods increases, they order orientationally at lower volume fraction because this maximizes their entropy. Based on calculations of the relative energy per particle for a monolayer of CdS rods aligned perpendicular and parallel to Si₃N₄ little change in alignment is expected due to enthalpic effects (see Supporting Material).

The interaction energy between the rod (both the nanocrystal and the ligands) and the substrate in solution also plays a role in rod self-assembly, as shown by its effect on alignment in Figure 3c (vdW energy calculations are in the Supporting Material). A strongly attractive interaction encourages rods to maximize their area of contact with the substrate by lying parallel to it. As this attraction is decreased, a stronger preference for perpendicular alignment is observed. Similar to Titov²⁷, we found that the substrate influenced alignment. However, our experimental results show that the alignment is not a simple function of the substrate Hamaker constant, and that in general alignment is not strongly dependent upon the substrate (see also Figure 4) over the range of interactions we considered. Based on theoretical analysis, we suggest that the ligands (neglected by Titov) play an important energetic role. The vdW energies calculated in solution are typically of the order of kT or smaller, i.e. small relative to thermal energy, primarily because the ligands prevent the crystalline cores from interacting strongly with each other and with the substrate. This result explains why perpendicular alignment is

only weakly substrate dependent. The inclusion of the ligands in our analysis also offers an explanation for the subtle dependence of alignment on the choice of substrate. If the Hamaker constant of the substrate is greater than that of the solvent then the ligands are effectively repelled by the substrate at close range. This effect leads to a non-monotonic dependence of the rod-substrate interaction energy on the substrate Hamaker constant, as shown by the curve in Figure 3c.

Our calculations also show that ligand-ligand and ligand-substrate interactions are large and dominant in the absence of solvation (100s of kT). While it is clear that self-assembly does not occur after drying is complete, fluctuations in solvent density near the liquid-vapor interface could activate these strong attractions in the late stages of assembly^{28,29}. The interaction energies calculated suggest that perpendicular alignment should be largely independent of the choice of nanocrystal material. Indeed, reports of self-assembly demonstrate vertical alignment of CdS ¹², $CdSe$ ¹⁵, $CdS-CdSe$ heterostructures¹⁴, Cu_2S ³⁰, Ag_2S ³⁰, and Au ³¹ rods. The visible film contraction and cracking that occurs at the final stage of drying is also consistent with the large increase in ligand vdW interactions that we calculate upon desolvation.

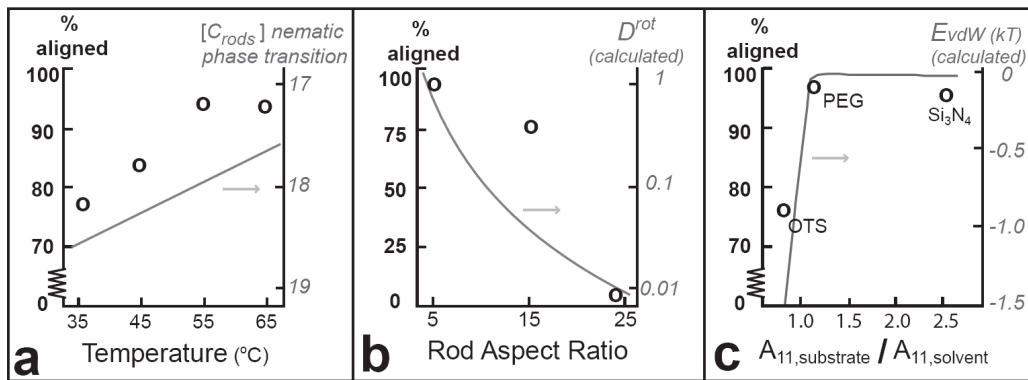


Figure 3. Entropy, enthalpy, and kinetics all contribute to self-assembly. a) An elevated temperature increases the percentage of vertically aligned rods (o's), and decreases the required rod concentration for a nematic (ordered) phase transition (line)²⁵. This temperature dependence demonstrates kinetic and entropic contributions to self-assembly. b) The dominant effect of assembly kinetics is seen by the strong dependence of alignment on rod aspect ratio; short rods align easily while long rods are more difficult to align (o's). This trend would be reversed if entropy or enthalpy were dominant. The calculated rotational diffusion constant (normalized to $D^{rot(AR=5)}$) similarly decreases with increasing aspect ratio (line). c) Enthalpic effect on assembly is demonstrated by using substrates with different Hamaker constants (A_{11}) and therefore different rod-substrate

interaction strengths. Substrates were silicon nitride TEM membranes, some functionalized with self-assembling monolayers (SAMs): octadecyltrichlorosilane (OTS) & polyethylene glycol (PEG). A stronger attraction (calculated as vdW interaction in solution) between the substrate and the rod surface (*line*) results in more horizontally oriented rods (**o**'s). Diffraction results were corroborated qualitatively with TEM images of each sample. Error bars fall within each data point. Identical nanocrystal samples and preparation procedures were used for each temperature and substrate study for consistency.

In summary, the strong trend counter to thermodynamic expectations that is achieved by aspect ratio variation (as compared to temperature or substrate variation) suggests that kinetics plays a dominant role in rod self assembly. While the analysis presented here provides valuable insight into this process, a complete description will need to address the kinetic interplay among evaporation, concentration, aggregation, deposition, and flow that ultimately determines film structure and particle orientation. Drying-mediated self-assembly is inherently a complex dynamical process that involves phase transitions in both nanorod and solvent density, i.e., slowly relaxing systems far from equilibrium.

Our quantitative exploration of factors affecting alignment allowed us to optimize assembly conditions and thereby vertically align nanorods on a variety of substrates (Figure 4); low aspect-ratio rods were used to aid the kinetics, and an increased temperature for a small improvement in vertical nanorod alignment. Because enthalpic interactions are dominated by ligands, making the rod-substrate interactions relatively weak, we were able to align rods on a range of substrates. Wide peaks in the ODF were observed for rough substrates (indium tin oxide (ITO) and rough silicon nitride (Si_3N_4); RMS roughness $\sim 1.2\text{nm}$ and 1.7nm respectively), while sharper peaks were observed for smooth substrates (Si_3N_4 RMS roughness 0.5nm), demonstrating that rough surfaces do not significantly disturb rod alignment, but merely broaden the orientation distribution; rough and smooth Si_3N_4 substrates alike had only 1-3% of rods oriented horizontally (within 20° of the substrate plane). Interestingly, the Si_3N_4 substrates with a PEG SAM (polyethylene glycol self-assembling monolayer) provided the best vertical alignment, with up to 95% of the rods vertically aligned, consistent with the vdW interaction data in Figure 3c. The variety of substrates on which rods have been demonstrated to self-assemble with a high

degree of alignment points further to the generality of our method; both rods and substrates of varying compositions can participate in the drying-mediated self-assembly described here.

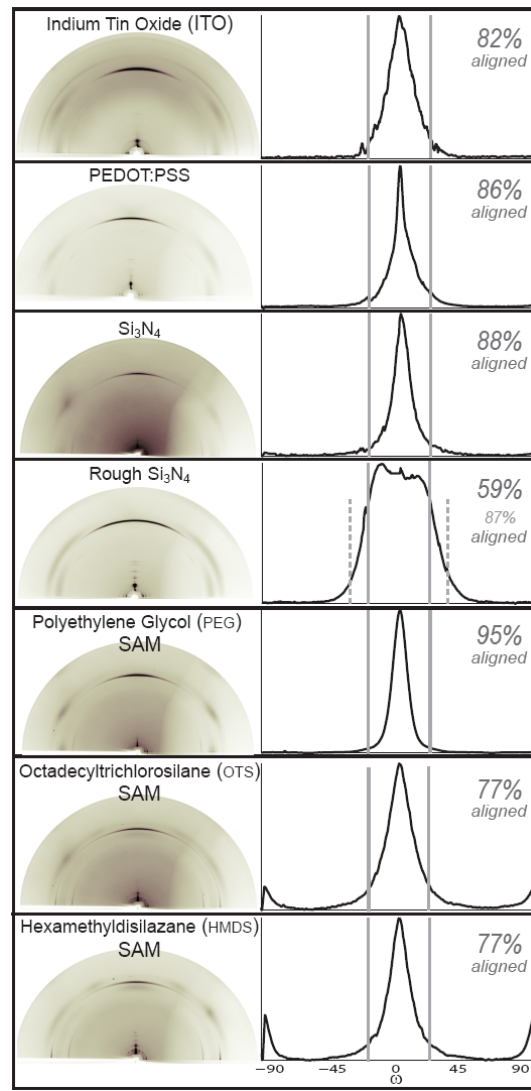


Figure 4. Substrate generality is shown: diffraction patterns and corresponding orientation distribution functions for each substrate. Percent vertical alignment (shown on right-hand side) is calculated by integration of the orientation distribution function between $\pm 20^\circ$. A rough substrate results in a wider angular distribution for aligned rods. On OTS and HMDS substrates, we can see significant tails indicating horizontally oriented rods. Substrates here are $\sim 7\text{mm}^2$. Nanocrystal sample used was identical for each substrate, for fair comparison.

We further show scaling of our technique to larger areas, achieving 96% alignment of the nanorods on a 1cm^2 substrate (Figure 5). By adapting techniques from photonic crystal assembly³² film quality was improved in terms of its uniformity in thickness and a reduction in crack size; the substrate was carefully cleaned and the

evaporation rate was reduced to $<1\text{mm/min}$ meniscus speed (across substrate). A substrate tilt angle of 5° provided a single meniscus extended across the substrate during drying, producing a uniform film of aligned nanorods across the entire area.

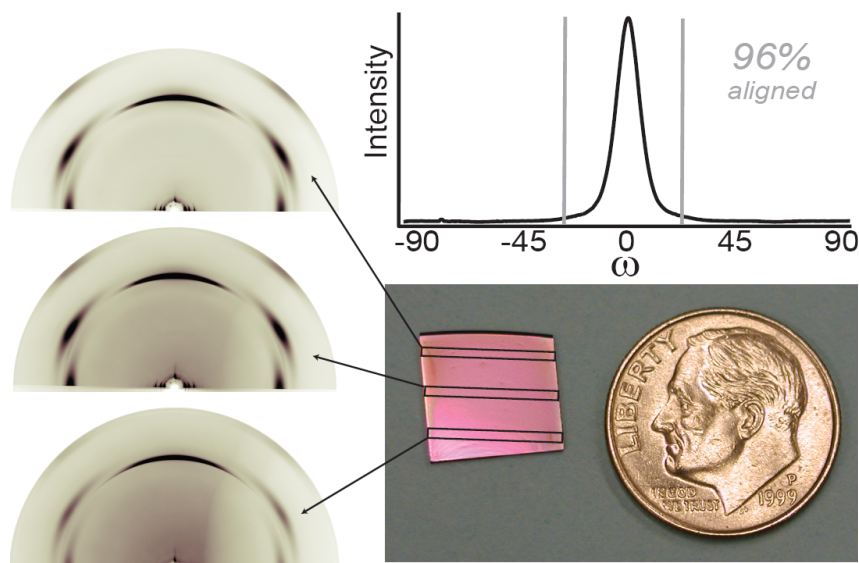


Figure 5. This self-assembly technique enables nanorod alignment on a device scale (1cm^2). Diffraction patterns corresponding to different areas on the substrate demonstrate uniformity across the film. Integrated intensity (ODF) from these diffraction patterns shows that we are able to achieve 96% vertical alignment on this silicon nitride substrate, pictured here next to a dime.

These large-area films comprise an assembly of many smaller domains. We found that in addition to vertical orientation, the rods in each of these domains were rotationally ordered (about their c-axis) with respect to each other. Selected area wide-angle electron diffraction shows that these rods are rotationally ordered in the plane of the film (with $\pm 15^\circ$ leeway for rotation about the c-axis presumably due to deformable ligands), forming a supercrystal in two dimensions (see Supporting Material Figure S5). Because wurtzite nanorods are known to have an approximately hexagonal cross section³³, their faceting might induce the rotational order observed. This result indicates that by probing an entire domain one could investigate nanoscale properties as a function of the crystal axis, currently impossible with colloidal nanorods randomly oriented either in solution or in dried films.

Further improvement in film quality will facilitate integration of these films in devices. Also, with further insight into kinetics, it may be possible to achieve alignment of rods with increasing aspect ratio. This in turn

would expand the applicability of this technique by allowing monolayer films of selectable thickness. We have characterized key self-assembly parameters, exploring the importance of enthalpy, entropy, and kinetics, and we suggest that kinetics is the dominant effect that can be modified by varying experimental parameters. This exploration led us to vertically align nanorods on many device-relevant substrates, and at the centimeter scale. Ultimately, this advance may play a critical role in the development of inexpensive, solution-processed optoelectronics with performance matching that of bulk semiconductor devices.

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Supporting Information

Experimental details, details of theoretical calculations, TEM, SEM and SAED images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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