Supporting Information

Asymmetric van der Waals Forces Drive Orientation of Compositionally Anisotropic Nanocylinders within Smectic Arrays: Experiment and Simulation

Benjamin D. Smith[§], Kristen A. Fichthorn,[†⊥] David J. Kirby,[§] Lisa M. Quimby,[§] Derek A. Triplett,[†] Pedro González,[‡] Darimar Hernández,[§] Christine D. Keating[§]**

Departments of Chemical Engineering,[†] Chemistry,[§] and Physics,[⊥] The Pennsylvania State University, University Park, Pennsylvania 16802

* To whom correspondence should be addressed. E-mail: keating@chem.psu.edu (C.D.K.); fichthorn@psu.edu (K.A.F.).

Present addresses: L. M. Q. – Skidmore College, Saratoga Springs, NY; D. A. T. –E.I. DuPont de Nemours and Company; B. D. S. – Juniata College, Huntingdon, PA

Contents.

Supporting Methods.

Surface Coatings**.** Nanowire surfaces were functionalized to provide electrostatic repulsion and prevent aggregation. Typically, nanowires were coated with a ~30 nm SiO_2 by a modified sol-gel method that is detailed in the text and can be found in the literature.[1,2] Other coatings used and shown in this supporting information were 2-mercaptoethanesulfonic acid (MESA) (Sigma), Poly(sodium 4-styrene-sulfonate) (PSS) (Aldrich), and thiolated DNA. MESA was coated by rinsing a volume of nanowires (at batch concentration) into the same volume of a 10 mg/mL MESA solution and vortexed for 2 hours. This was followed by three rinses in water before assembly. PSS (70,000 g/mol) coatings followed the same procedure as the MESA coating; however, a 10 mg/mL PSS solution was used instead of the MESA solution. Lastly, DNA coated wires were prepared following previously published reports.[3] Briefly, thiolated DNA (5′ to 3′ HS-C_6H_{12} AAA AAA AAA A) was purchased from Integrated DNA Technologies. It was received as a disulfide and was cleaved by reaction with 100 mM dithiothreitol (DTT) for 30 min in a 0.1 M phosphate buffer (pH 8.3). The DNA was then purified using CentriSpin 10 columns (Princeton Separations). From a stock concentration, 100 μL of a nanowire suspension (batch concentration) were rinsed into a pH 7.0 phosphate buffer (with 0, 20, or 1000 mM NaCl). Based on known surface coverages for this attachment, an excess of DNA was used to cover the surface.[4] This solution was rotated for 30 minutes. After rinsing with buffer, the wires were resuspensed in deionized water for assembly.

Nanowire Assembly. Nanowires were assembled as described in the methods section of the text with the following changes. Assembly chambers were prepared and sealed away from the microscope (a silicone spacer [Invitrogen] in between a microscope slide and a cover slip) and were inverted for imaging. These experiments also used a larger silicone spacer (0.64 cm^2) so 100 μL of ~1.5×10^9 nanowires/mL were used to create the same surface coverage studied in the main text. SiO_2 coated nanowires used in Figure 1 were only assembled for 1-3 h while all others explored were allowed to rest on the microscope stage overnight (~15 hours) before imaging.

Imaging and Image Analysis**.** Imaging and image analysis were performed as described in the main text. Images were acquired on a Nikon TE200 or Nikon TE300 inverted microscope with Hg or Xe arc lamp respectively with a CoolSnap HQ camera. Images collected on the TE300 microscope employed a 430 nm filter to improve the contrast between Au and Ag in the resulting images.

References

1. Smith, B. D.; Kirby, D. J.; Ortiz Rivera, I.; Keating, C. D. Self-Assembly of Segmented Anisotropic Particles: Tuning Compositional Anisotropy to Form Vertical or Horizontal Arrays. *ACS Nano* **2013**, *7*, 825-833.

2. Smith, B. D.; Kirby, D. J.; Keating, C. D. Vertical Arrays of Anisotropic Particles by Gravity-Driven Self-Assembly. *Small* **2011**, *7*, 781-787.

3. Cederquist, K. B.; Stoermer Golightly, R.; Keating, C. D. Molecular Beacon – Metal Nanowire Interface: Effect of Probe Sequence and Surface Coverage on Sensor Performance. *Langmuir* **2008**, *24*, 9162-9171.

Supporting Tables.

Supporting Table 1. Analysis of six images of silica-coated Au-Ag nanowires that correspond to the assembly shown in Figure 1.

Image	Number of Wires				S_3
	↑↑↑	↑↑↓	↑↓↑	Total	
1	270	156	67	493	0.41
2	387	135	56	578	0.57
3	382	219	95	696	0.41
4	135	152	80	367	0.15
5	112	155	69	336	0.13
6	64	101	48	213	0.08
Total	1039	510	218	1767	**0.35**
Average					**0.3 ± 0.2**

Assemblies were imaged after at least 1 h. Wire and segment lengths were estimated based on plating times used. This sample had three images (1, 2, 3) that displayed exceptionally high S_3 values. Images 2 and 5 are shown in Figure 1 in the main text.

Supporting Table 2. Dimensions of nanowire sets used in this work.

Nanowire	L_1 (μm)	L_2 (μm)	L_3 (μm)	Diameter (nm)	Silica Shell (nm)
Au-Ag	2.4 ± 0.2	2.3 ± 0.2	0.10 ± 0.03	290 ± 40	38 ± 4
PENs	2.4 ± 0.2	1.3 ± 0.1	1.3 ± 0.1	270 ± 40	28 ± 4

Dimensions of nanowires as determined by measuring transmission electron micrographs. For the Au-Ag nanowires, L_1 is L_{Au}, L_2 is L_{Ag}, and L_3 is the Au cap. For the PENs L_1 is L_{2Au}, L_2 is L_E, and L_3 is L_{Au}.

Variations in Nanowire Coatings.

For comparison to **Table 1** in the main text gives the data for SiO_2 coated Au-Ag nanowires (2 μm segments). All wires described below had the same size, as estimated by plating times used.

Supporting Table 3. Analysis of MESA-Coated Au-Ag Nanowires

Sample	Number of Wires				S_3
	↑↑↑	↑↑↓	↑↓↑	Total	
1-1	178	253	99	530	0.15
1-2	202	319	112	633	0.14
1-3	152	247	98	497	0.11
1-4	170	296	127	593	0.07
1-5	189	293	116	598	0.12
1-6	205	292	106	603	0.16
Total	**1096**	**1700**	**658**	**3454**	**0.13**
Average					**0.13 ± 0.03**
2-1	135	251	113	499	0.04
2-2	168	243	100	511	0.13
2-3	186	271	123	580	0.11
2-4	155	261	95	511	0.12
2-5	141	262	83	486	0.12
2-6	161	259	80	500	0.16
Total	**946**	**1547**	**594**	**3087**	**0.11**
Average					**0.11 ± 0.04**

Images were collected after assembling overnight. Two separate batches of wires were tested (noted here as batch 1 and 2; six separate assembly experiments were performed with each of the two batches of wires).

Supporting Table 4. Analysis of DNA-Coated Au-Ag Nanowires

DNA Coverage	Sample	Number of Wires				S_3
		↑↑↑	↑↑↓	↑↓↑	Total	
Low	1	709	798	330	1837	0.21
	2	405	426	163	994	0.24
	3	401	442	171	1014	0.23
Medium	1	361	518	227	1106	0.12
	2	285	421	231	937	0.06
	3	286	423	161	870	0.14
High	1	989	1173	402	2564	0.23
	2	866	1058	381	2305	0.21
	3	442	603	244	1289	0.15
	Total	**4744**	**5862**	**2310**	**12916**	**0.19**
	Average					**0.18 ± 0.06**

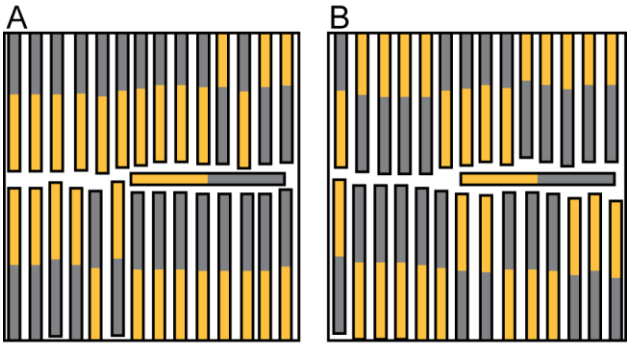
Assemblies were imaged after at least 1 hour. Low, medium, and high DNA coverages are approximately 1, 10, and 100×10^{11} DNA/cm^2 as reported in reference 4.

Supporting Table 5. Analysis of PSS-Coated Au-Ag Nanowires

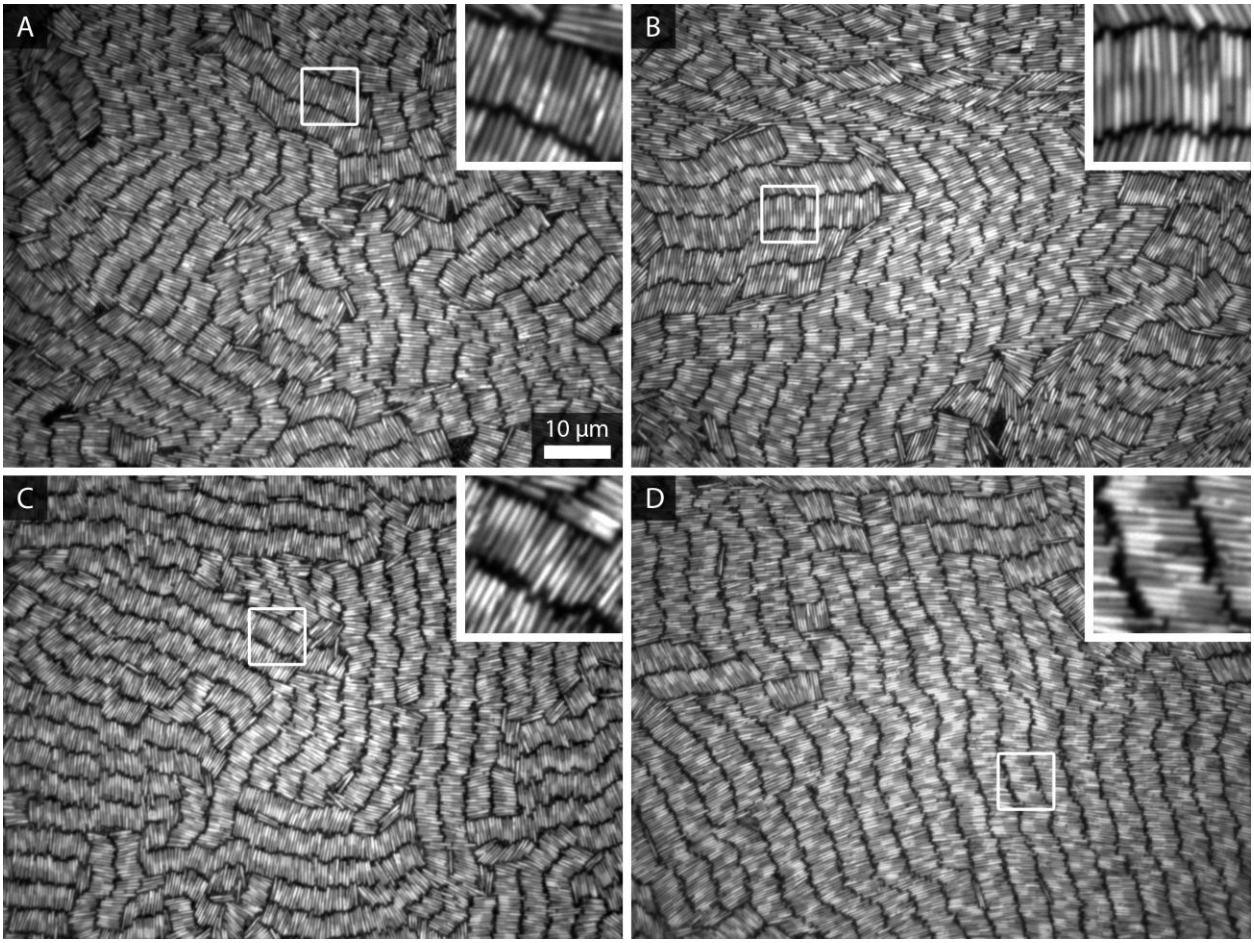
Sample	Number of Wires				S_3
	↑↑↑	↑↑↓	↑↓↑	Total	
1	232	468	146	846	0.10
2	149	293	114	556	0.06
3	184	297	96	577	0.15
4	212	356	150	718	0.09
5	208	310	103	621	0.17
6	236	395	127	758	0.14
Total	**1221**	**2119**	**736**	**4076**	**0.12**
Average					**0.12 ± 0.04**

Images were collected after assembling overnight.

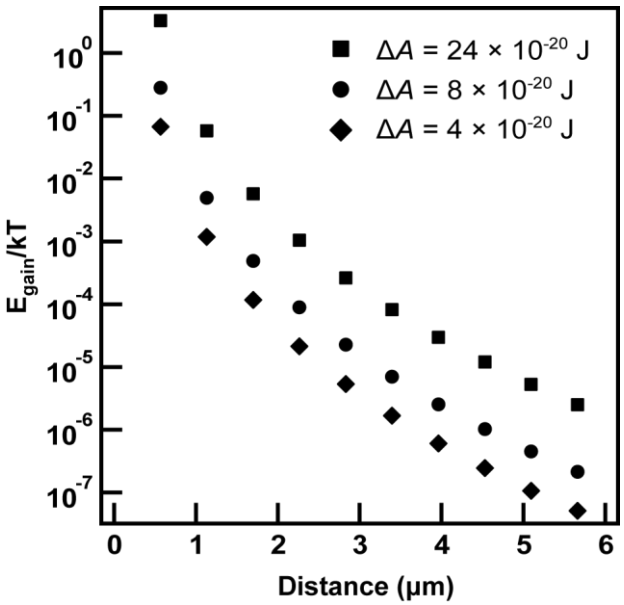
Supporting Figures



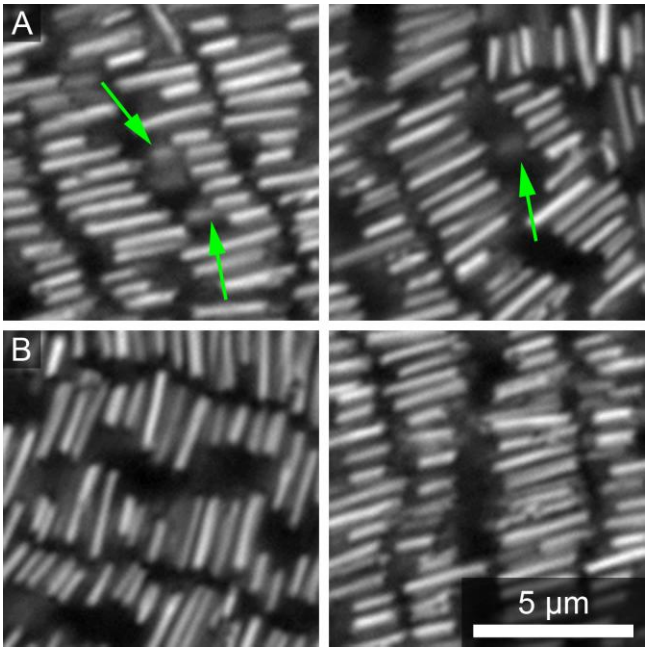
Supporting Figure S1. Illustration of two assemblies with identical order parameters. Though both illustrations have S_3 = 0.5 they appear visually distinct since A includes nanowires with both neighbors oriented oppositely, while B has none.



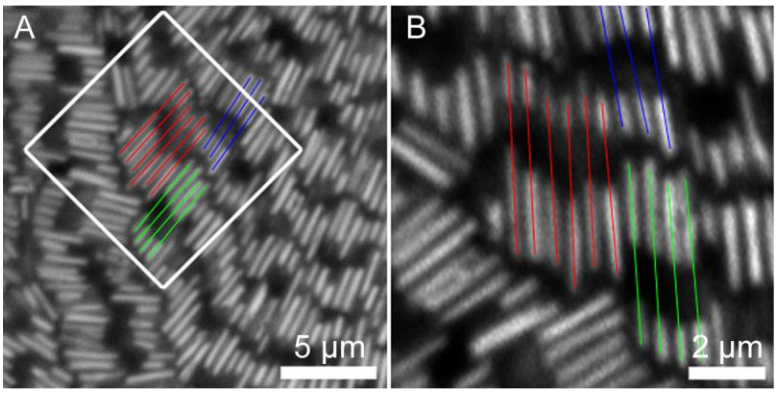
Supporting Figure S2. Representative optical micrographs of Au-Ag nanowire assemblies with different surface coatings. A) SiO_2, B) MESA, C) DNA [1000 mM NaCl coating condition], D) PSS. Analysis of complete assembly experiments can be found in Table 1 and Supporting Tables 3-5.



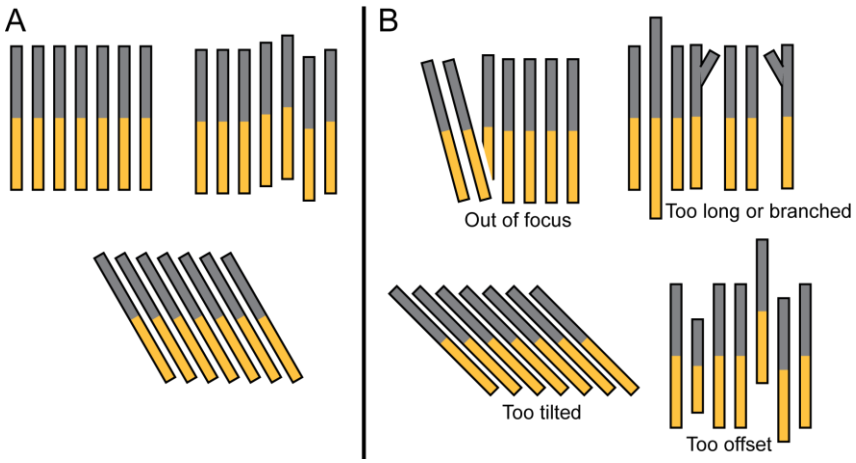
Supporting Figure S3. Plot showing the energy gain E_{gain} relative to kT for a pair of antiparallel wires to become parallel. Three traces are shown for ΔA corresponding to simulations run. Each point represents a neighboring distance (ranging from the first to the tenth neighbor) within a row of a nanowire array corresponding to the base-case experimental parameters.



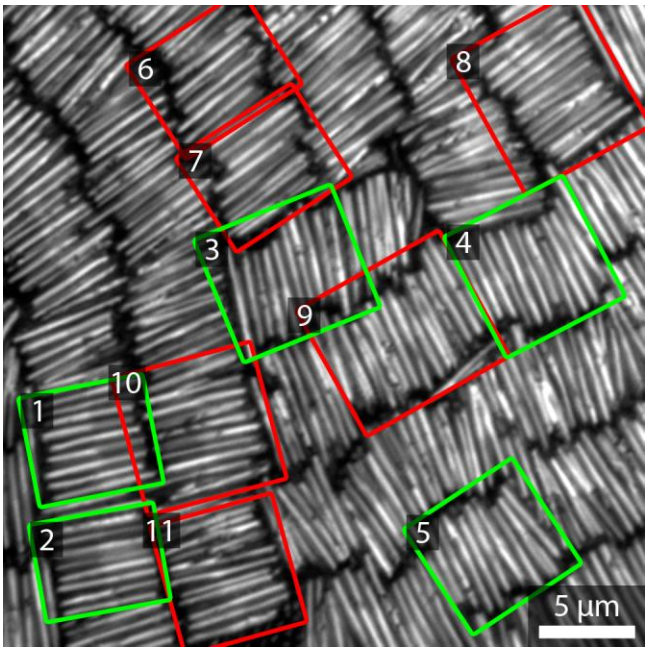
Supporting Figure S4. Transparent etched segments in PENs enable particles in an upper layer to be viewed. The two frames in A show portions of PENs in a second layer that are visible through the etched silica segment of the PENs in the lower layer (green arrows). These PENs can be seen because they are aligned differently than the bottom layer (i.e. their gold segments are above the transparent etched segments of the PENs under them). Frames in B show other regions of the assembly where no PENs in the upper layer are visible, indicating that any PENs in an upper layer are oriented the same way as the lower layer.



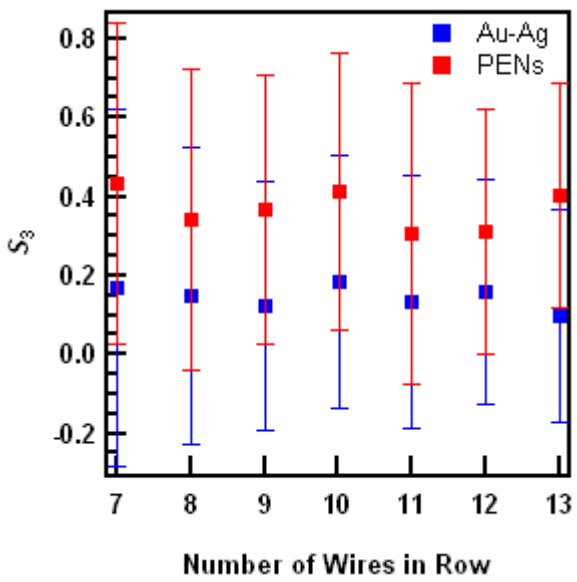
Supporting Figure S5. Image A) and expanded image B) of alignment between rows of nanowires. Red highlighted particles form the main row. The large end of the green highlighted particles aligns with the large ends of the main row. The small ends of the main row are aligned with the small ends of the blue highlighted nanowires.



Supporting Figure S6. Illustration of nanocylinder assemblies observed experimentally. The assemblies shown in A represent acceptable smectic rows of cylinders that were used for S_3 analysis. The regions shown in B represent defects in the formation of a well ordered smectic row. During analysis we classified these regions as poorly smectic and they were rejected from S_3 characterization measurements. The Methods section in the main text describes how regions were selected.



Supporting Figure S7. Selected area of a Au-Ag nanowire assembly. Regions highlighted in green (1-5) were used for data analysis of S_3. Regions highlighted in red (6-11) are areas that appear to be smectic rows but were rejected for analysis for any of the reasons illustrated in Supporting Figure S6. Box 6: Row is too tilted. Box 7: Row contains offset wires and out of focus wires. Box 8: Row contains out of focus and branched wires. Box 9: Row contains branched wires. Box 10: Row contains out of focus, branched and offset wires. Box 11: Row contains out of focus and branched wires. The Methods section in the main text describes how these regions were selected.



Supporting Figure S8. Plot showing the relation of S_3 value to the size of assembly areas. At least 30 regions were examined for each data point. Error bars show standard deviation (note that due to small data set, uncertainty is larger for these data than the S_3 values averaged over all row lengths within an experiment).