

Tuning the 1D to 2D Transition in Lepidocrocite Titanate Nanofilaments via Polymer Wrapping

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Abstract

Recently, a solution-based method was developed to synthesize sub-nm thin one-dimensional (1D) lepidocrocite (1DL) titanium oxide-based nanofilaments as a colloidal suspension. When converted into the solid-state, these 1DL nanofilaments self-assemble into two-dimensional (2D) layered structures. Herein, we show how a polymer – branched polyethyleneimine (bPEI) – can be used to wrap 1DL surfaces and arrest this 1D–2D structural transition. X-ray diffraction confirmed that the polymer molecules coated onto individual 1DL surfaces. More interestingly, the bPEI-coated 1DLs form a hexagonal columnar liquid crystalline structure in the solid-state, and the inter-1DL distances can be readily tuned from 1.66 to 3.00 nm by controlling the polymer to 1DL volume ratio. Combining the XRD results and DFT calculations,

we conclude that the 1D nanofilaments, on average, are comprised of 2x2 edge-shared TiO_6 octahedra, roughly 0.6 nm in diameter. The tunable liquid crystalline phase could open new opportunities to realize 1DL in multiple applications.

Introduction

Titania (TiO_2) nanomaterials have found profound applications in our daily lives, ranging from catalysis to paints, energy storage, sensors, drug delivery, etc.^{1,2} The more oxygen rich family of titanates, with layered titanates (LTs) being of particular interest, have shown a similar range of applications.³⁻⁵ LTs, akin the materials discussed herein, require an interlayer cation to balance the additional negative charge provided by the additional oxygen in the backbone.^{6,7} Titanium oxide nanoparticles and nanosheets have been extensively investigated, while one-dimensional (1D) titania received less attention.^{6,8-10} The reported 1D morphologies of titania and LTs include nanotubes¹¹, nanorods¹², and nanoribbons¹³, and they can be synthesized by various methods primarily requiring hydrothermal environments, various additives, or extensive post-processing.^{11,12,14,15}

Most recently, a simple, one-pot solution-based method was developed to synthesize sub-nm, 1D LT filaments as shown schematically in Scheme 1A.^{16,17} These nanofilaments are hereafter labelled 1D lepidocrocite or, 1DL. Their synthesis relies on the dissolution of Ti-containing precursors in a high pH environment. For example, concentrated (25% w/w in water) tetramethylammonium hydroxide (TMAOH) is used to supply both the high pH and large cation as a templating agent¹⁷. Alkali bases, under the same conditions, do not result in a similar product¹⁸. Note, that in the literature, there are many reports of 1D titania or LTs.^{10-12,19,20} What sets this work apart is that 1DLs are the first to see a major increase in band gap energy, as a result of quantum confinement along two dimensions.²¹ Many of the promising applications of 1DLs, such as

adsorptive²²⁻²⁵ and photocatalytic^{22,26} properties, are associated with their high specific surface areas and the ultra-thin primary filament structure. Theoretically, one gram of 1DL spans 600 million kilometers and covers $\approx 500 \text{ m}^2$.

Based on the processing method, both porous mesoscale particles²⁴ or an extremely stable colloidal suspension can be obtained²⁷. Much of the work on 1DLs, including the results presented herein, focus on the 1DL colloidal suspension. During early work, the cross-section of a 1DL nanofilament building block was assumed as $0.5 \times 0.7 \text{ nm}$ ¹⁷. The 0.5 nm dimension is unimpeachable since it is based on X-ray diffraction (XRD) patterns and high-resolution transmission electron microscope, HRTEM, micrographs^{17,27,28}. The 0.7 nm dimension, however, has been more speculative and simply based on the shape isotropy of the 1DLs in HRTEM images. Upon drying, lateral aggregation of 1DL occurs, and the 1DLs merge and form 2D layered structures based on XRD, with the layer normal being identified as the $[0k0]$ direction. **Scheme 1A,B** shows schematic representations of 1DL and 2D structures viewed from different crystallographic axes. It follows that a major goal of this work is retaining the 1D nature of the primary structure in the solid-state is scientifically intriguing and could be technologically of high impact. Polymers, including natural and synthetic macromolecules, have been routinely used to modify nanoparticle surfaces for dispersion and assembly purposes.^{29,30} For example, polymers can be chemically grafted onto nanoparticle surfaces to form polymer brushes.^{29,31,32} They can also wrap onto 1D nanotube or nanowire surfaces via physical interaction.^{29,31,33} We hypothesize that a polymer coating on the 1DL nanofilament in aqueous solution could sterically prevent the inter-filament merging (**Scheme 1C**).

In this work, bPEI was chosen to form the polymer coating on 1DL nanofilaments because it is a water soluble polymer and the branched architecture increases the primary amine content, enabling strong and efficient interaction with the titania nanoparticle surfaces.³⁴ The main variable used was the polymer to 1DL weight ratio. Our results show that ordered bPEI-1DL hybrids can be readily formed using solution blending. The bPEI molecules effectively interact with the 1DL surfaces, arresting their transition to a 2D layered structure. More interestingly, upon drying, these bPEI-coated 1DLs self-assemble into hybrid columnar hexagonal (Col^{hex}) liquid crystalline (LCs) phases, with an average primary 1DL diameter filament of ~ 0.6 nm. The inter-filament distance can be readily tuned by varying the bPEI to 1DL ratio. The structural evolution from 1D to 2D, or lack thereof, was systematically investigated.

Results and Discussions

The 1D-2D transition

The hybrids were prepared by mixing a 1DL-water suspension and an aqueous PEI solution at precalculated mass ratios. The resulting mixtures were then poured into petri dishes, and solid films were formed as the solvent evaporated. The bPEI to 1DL mass ratio, m , was varied from 0 to 19, and $m = 0$ indicates neat 1DL. Henceforth, the composite samples are denoted as $mbPEI$ -1DL. **Fig. 1A** presents typical, low 2θ angles, XRD patterns of a neat 1DL along with 0.1bPEI-1DL and 0.2bPEI-1DL. The XRD pattern has characteristic diffraction peaks at 2θ of 7.69° , 15.44° , and 23.22° , following a ratio of 1:2:3 (black arrows in **Fig. 1A**). This suggests that the packing of the neat 1DL is 2D with an inter-layer distance of 1.15 nm. The XRD patterns of 0.1bPEI-1DL and pristine 1DL are similar, showing multiple diffraction peaks with 2θ ratios of 1:2:3, confirming

the 2D structure in 0.1bPEI-1DL as well. Note that the main diffraction peak of 0.1bPEI-1DL slightly downshifts from 7.71° (d-spacing of 1.146 nm) to 7.65° (d-spacing of 1.16 nm) and becomes asymmetric with stronger intensity developed on the peak's low angle shoulder. This shoulder is stronger in the 0.2bPEI-1DL XRD pattern (bottom pattern in **Fig. 1A**) at 2θ of $\sim 5.15^\circ$ (blue arrow in the figure), while the main peak still shows 2D characteristics. The shoulder peak clearly suggests the development of a new structure.

The XRD pattern of the 0.5bPEI-1DL sample (Fig. 1B), is significantly different from **Fig. 1A**. Here a series of diffraction peaks are observed at the 2θ angles of 5.61° , 9.71° , 11.22° , and their relative ratios are $\sim 1:\sqrt{3}:2$. Relatively weak scattering at $\sim 14.84^\circ$, and 16.83° can also be seen, and their relative ratios to the primary peak are $\sim 1:\sqrt{7}:3$. This pattern represents a characteristic 2D hexagonal packing, and the diffraction peaks can be assigned as (01), (11), (20), (21) and (30), respectively. The structure can, therefore, be identified as a hexagonal columnar (Col^{hex}) LC phase, where polymer-coated 1DLs pack into a 2D hexagonal lattice. Such Col^{hex} phases are often observed in small molar mass discotic LCs and polymer LCs.³⁵⁻³⁹ In the present case, the polymer molecules wrap the 1DLs, and self-assemble into a hexagonal packing. Based on the (10) d-spacing of 1.44 nm (from $2\theta = 5.61^\circ$), the 2D hexagonal unit cell dimension a^{hex} can be calculated as 1.66 nm. Inset in **Fig. 1B** is a schematic of the Col^{hex} phase viewed along the hexagonal axis. Here the inter-filament space is occupied by bPEI (not shown for clarity). Since the 1DLs are coated with bPEI, it is reasonable to assume that they are axially symmetric, *i.e.*, the in-plane orientation of the 1DL in the hexagonal lattice is random, as indicated in the scheme. Note that individual 1DLs are 1D crystals of TiO_6 octahedra, as shown in **Scheme 1A**.²⁴ Therefore, the 0.5bPEI-1DL structure is hierarchical, comprising an inter-filament Col^{hex} packing at the 1-2 nm

length (inset in **Fig. 1B**) scale and an intra-filament 1D crystalline structure with a period of 0.38 nm, which is a lattice parameter of the 1DLs.²⁸

Since the original 1DL samples contained residual TMAOH, thermogravimetric analysis (TGA) was conducted to estimate the solid content (**Fig. S1**). The TMAOH content in pristine 1DL is ~ 9.7 wt.%, and the TMAOH is assumed to be retained in the final hybrid film since the solution blending/evaporation method was utilized to prepare the sample. The organic-to-inorganic phase ratio in the 0.5bPEI-1DL therefore can be estimated to be $(0.5+0.097)/(1-0.097) = 0.66$. Assuming the bPEI and 1DL densities are 1.03 g/ml and 3.96 g/ml, respectively, the volume ratio can be estimated to be $\phi = v_{org}/v_{in} = 2.54$. The 1DL density was estimated based on the DFT-obtained 1DL structure and is similar to the density of anatase²⁸. Assuming a round cross-section of 1DLs, the 1DL filament diameter, d_{1DL} , and the bPEI layer thickness between the 1DL, d_{PEI} , can be calculated based on

$$d_{1DL} = \frac{a^{hex}}{\sqrt{\frac{v_{org}}{v_{in}} + 1}} \quad (\text{eq. 1})$$

and

$$d_{PEI} = a^{hex} - d_{1DL} \quad (\text{eq. 2}).$$

In the 0.5bPEI-1DL sample, $a^{hex} = 1.66$ nm, we obtain a d_{1DL} of 0.64 nm and d_{PEI} of 1.02 nm (see inset **Fig. 1B** and **Table 1**). The d_{1DL} of 0.64 nm is consistent with the 0.5×0.7 nm² cross-sectional dimension based on DFT calculations.

At this juncture it is instructive to summarize our DFT calculations. Since the 1DL structure is that of lepidocrocite, they must be comprised of edge-sharing TiO₆ octahedra. It follows that their width in the c-direction has to be multiples of these octahedra, which begs the question: Is the width comprised of 2 or 3 TiO₆ octahedra? The DFT calculations yield values of 0.6 and 0.9 for 2 and 3 TiO₆ structures, respectively. Based on the totality of the results shown herein, there is

little doubt that the answer is 2. This is a crucial result that cannot be emphasized enough since it unambiguously sets a lower limit on the number of TiO_6 octahedra along the c -direction to be 2. The 1DLs cross-sections are thus comprised of 2×2 TiO_6 octahedra $\approx 0.6 \times 0.6 \text{ nm}^2$ in cross-section.

Furthermore, since we assume the 1DLs to be axially symmetric in the lattice and Col^{hex} is centrosymmetric ($P6mm$ space group), we can estimate the electron density map using the XRD pattern shown in **Fig. 1B**, without detailed phase information (see SI for detailed procedure).^{40,41} The hexagonal symmetry of the 1DLs can be reconstructed, as shown in **Fig. 1C**. The high electron density region, attributed to 1DL, is approximated 0.6 nm in diameter (see **Fig. S2**), which is consistent with the density estimation results presented in **Table 1**. A top view of a DFT-obtained 1DL cross-section is shown as a small inset in center of **Fig. 1C**. Given the several simplifying assumptions made to generate **Fig. 1C**, the match has to be considered excellent.

These observations confirm our conjecture that bPEI molecules coat individual 1DLs and arrest the 1D-2D transition previously observed. In **Fig. 1D**, we show the reconstructed electron density map of neat 1DL based on the strongest layer scattering peaks. The layer thickness is 0.53 nm, which is consistent with the TiO_2 distance along the b axis. The organic layer thickness therefore is 0.62 nm. One layer of DFT-obtained 2D lepidocrocite structure is included in **Fig. 1D** to demonstrate the consistent TiO_2 layer thickness obtained from the electron density reconstruction and the simulation. **Table 1** summarizes the characteristic Col^{hex} dimension, d_{10} , as a function of m . Also listed are the 1DL dimensions, $d_{1\text{DL}}$, obtained from d_{10} (column 9 in **Table 1**).

Table 1. XRD characterization of the Col^{hex} structure of $m\text{bPEI}$ -1DLs.

Sample	m^1	ϕ^2	$(10)^3$	$(11)^3$	$(20)^3$	$d_{(10)} \text{ (nm)}$	$a^{\text{hex}} \text{ (nm)}$	$d_{1\text{DL}} \text{ (nm)}$	$d_{\text{PEI}} \text{ (nm)}$	$\xi^4 \text{ (nm)}$	n
0.5bPEI-1DL	0.5	2.5	5.61 (5.61)	9.70 (9.70)	11.22 (11.20)	1.44	1.66	0.64	1.02	2.6	1.8

0.8bPEI- 1DL	0.8	3.8	4.81 (4.81)	8.32 (8.32)	9.62 (9.67)	1.84	2.12	0.72	1.40	3.2	1.7
0.9bPEI- 1DL	0.9	4.2	4.02 (4.02)	6.96 (6.83)	8.04 (7.95)	2.20	2.54	0.83	1.71	3.5	1.6
1.2bPEI- 1DL	1.2	5.5	3.81 (3.81)	6.59 (6.63)	7.62 (7.72)	2.32	2.68	0.80	1.88	4.4	1.9
1.5bPEI- 1DL	1.5	6.8	3.40 (3.40)	5.88 (5.88)	6.80 (6.80)	2.60	3.00	0.83	2.17	5.0	1.9

1. *bPEI to 1DL mass ratio*
2. *bPEI to 1DL volume ratio*
3. *2θ of diffraction peaks. In each sample, top and bottom row numbers are from calculations and experiments, respectively. Only first three diffraction peaks are listed.*
4. *From Scherrer equation.*

As noted above the primary filament thickness or 'diameter' is ~ 0.6 nm. To further support this result in real space, atomic force microscopy (AFM) was utilized. Neat 1DL and 0.5bPEI-1DL solutions were spun cast onto glass slides for AFM imaging. The fast spin coating process was utilized to avoid the 1D-2D transition during sample preparation. As shown in **Figure 1E,F**, the thinnest filament height of 1DL and 0.5bPEI-1DL is 0.8 and 1.5 nm, respectively. The 0.8 nm thickness, rather than 0.6 nm, is most probably due to the coating of TMAOH on the 1DL surfaces, and the increased size to 1.5 nm in 0.5bPEI-1DL is attributed to the bPEI coating. These results are, again, consistent with the Col^{hex} structural dimensions determined from the XRD results as shown in **Table 1**, further confirming that the polymer wrapping did significantly alter the 1DL self-assembly pathways.

As the Col^{hex} was formed by the bPEI wrapping around the 1DLs, we further hypothesized that the structure dimension can be tuned by controlling m . To this end, a series of samples, with m up to 19, were prepared. **Figure 2A** shows the XRD results for 0.5, 0.8, 0.9, 1.2 and 1.5bPEI-1DL samples. Similar multi-diffraction peaks can be seen in all these samples, with the main peaks gradually downshifting with increases in bPEI content. Detailed analysis confirms that all the

patterns follow a $\sim 1:\sqrt{3}:2:\sqrt{7}:3$ 2θ ratio, suggesting that they are Col^{hex} structures. The d -spacings of these diffraction peaks are listed in **Table 1**, along with their indices following the Col^{hex} structure. As m increases from 0.5 to 1.5, $d_{(10)}$ increases from 1.437 nm to 2.48 nm, and the unit cell dimension, a^{hex} , increases from 1.66 nm to 2.86 nm (**Fig. 2B**). Using Eqs. 1 and 2, d_{IDL} and d_{PEI} for all the samples can be estimated. The d_{IDL} values are approximately 0.64, 0.72, 0.83, 0.80, and 0.83 nm, while d_{PEI} is 1.02, 1.40, 1.71, 1.89, and 2.17 nm, respectively (**Table 1**). The 1DL filament size increases slightly – from 0.6 nm to 0.83 nm – while the inter-1DL distance doubles as m increases from 0.5 to 1.5. **Fig. S3** shows the reconstructed electron density map of the 1.5bPEI-1DL sample. Not surprisingly, the structure is similar to that shown in **Fig. 1C**.

Based on the full width of half maximum (FWHM) of the (10) diffraction peaks, the crystallite correlation size, ξ , can be estimated using Scherrer equation, viz. $\xi = (K\lambda)/(\beta \cos \theta)$, where K is the shape factor, λ is the X-ray wavelength, and β is the FWHM. The (10) correlation lengths, $\xi_{(10)}$, are listed in **Table 1**, along with the correlation units $n = \xi_{(10)} / d_{(10)}$. In all Col^{hex} structures, the $\xi_{(10)}$ value gradually increases from 2.6 nm to 5.0 nm as m increases from 0.5 to 1.5. However, the correlation units n maintains approximately 2, indicating the relatively poor ordering. To compare, in the 0.1bPEI-1DL samples where the 2D structure was observed, ξ was estimated to be 8.02 nm, and $n \sim 6.9$, indicating that the 2D structure maintains a longer-range order.

The structural evolution with increased bPEI contents was followed using SEM imaging, shown in **Figs. 2C-J**. The apparent stacking of 2D sheets is seen in neat 1DL (**Fig. 2C,D**) and are consistent with previous reports.²⁴ The sheets are parallel to the film surface, and there are thin fibrils at the edge of the tips (arrows in **Fig. 2C,D**), suggesting sheet formation is likely related to the aggregation of filaments. Similar 2D sheets are clear in 0.1bPEI-1DL (**Figs. 2E,F**) samples, but absent in the 0.5bPEI-1DL (**Fig. 2G,H**) and 0.8bPEI-1DL (**Fig. 2I,J**) samples. In the 0.5bPEI-

1DL sample, a layer of coating appears on the film surface, and in 0.8bPEI-1DL, the image seems formed by 1D materials coated with polymers, and the film is less dense. The SEM observations, therefore, further confirm the arrest of 2D structure formation in 0.5bPEI-1DL and 0.8bPEI-1DL.

The morphological features of these hybrid Col^{hex} solids were further studied using polarized light microscopy (PLM). **Figure 3A** shows, from left to right, respectively, typical PLM images of samples 0.1PEI-1DL, 0.5bPEI-1DL, 1.5bPEI-1DL and 5bPEI-1DL. Images for the complete sample set can be found in **Fig. S4**. Referring to **Fig. 3A**, the 0.1PEI-1DL sample (leftmost) shows strong birefringence from both the 1DL crystals and the 2D structure. Note that in the LC terminology, the 2D structure can be viewed as a smectic phase. The LC texture does not change significantly in 0.5bPEI-1DL when the materials enter the Col^{hex} phase region, while it becomes significantly weaker in the 1.5PEI-1DL samples, which is attributed to the high polymer content (87.1 vol.%). When the bPEI content is further increased in 5bPEI-1DL (95.6 vol.%), birefringence completely disappears, suggesting an isotropic phase. The formation of the latter is confirmed by XRD patterns, shown in **Fig. 3B**, for the 5bPEI-1DL and 19bPEI-1DL samples. The diffraction pattern shows a broad hump at 2θ angles of $\sim 5^\circ$. The broad 2θ range of the scattering hump and the lack of high-order diffraction peaks suggest that the 1DLs in these two samples are disordered, consistent with the PLM observation (**Fig. S4**). This is not surprising since the volume fraction of 1DLs in these composites, 4.4 vol.% and 1.2 vol.%, respectively, are quite low.

Figure 3C summarizes the structural evolution of the m bPEI-1DLs hybrid samples. First, when m is 0.1 and 0.2 (**Fig. 1A**), a 2D structure is seen, and the layer spacing remains relatively constant. Secondly, when m is 0.5 – 1.5, a Col^{hex} structure is formed, and the hexagonal dimension gradually increases with m . Note that since the material is formed by coating inorganic 1DLs with

polymers, it can be characterized as hybrid inorganic/organic solid with a Col^{hex} LC symmetry. Solid “liquid crystals” have been conventionally discussed in biomolecules such as DNA and rigid polymers.⁴² The bPEI-1DL hybrid presents a new hybrid LC solid with a Col^{hex} structure. Finally, increasing m to 5 and 19 leads to an isotropic phase where no clear 1DLs order is observed.

Conclusions

We have successfully utilized bPEI to coat ultra-thin 1D sub-nm filaments to arrest the spontaneous 1D-2D transition. As the bPEI to 1DL mass ratio increases from 0.1 to 19, the bPEI-1DL hybrids go from a 2D structure to a Col^{hex} LC, before entering an isotropic phase. The Col^{hex} lattice dimension can be tuned by the mass ratio, varying from 1.66 nm in 0.5bPEI-1DL to 3.00 nm in 1.5 bPEI-1DL. While the lattice parameter doubled from 0.5bPEI-1DL to 1.5 bPEI-1DL, the average 1DL diameter increased moderately from 0.64 nm to 0.83 nm, and the (10) correlation units remained at ~ 2 . The isotropic phase was observed when the bPEI to 1DL mass ratio exceeded 5. The polymer wrapping approach confirms the true 1D nature of the 1DLs, and these hierarchically ordered bPEI-1DL hybrids could find applications such as energy storage, water remediation, C capture, and catalysis, among others. Lastly, when our DFT calculations are compared to the results obtained herein, we can, for the first time, confidently conclude that the minimum cross-section of the 1DLs is comprised of 2x2 edge-sharing TiO_6 octahedra.

Experiment Procedures

Resource Availability

Lead contact

Further information in this study and requests regarding resources and reagents should be directed to and will be fulfilled by the lead contact, Christopher Y. Li (Chrisli@drexel.edu).

Materials availability

All structural data and information generated in this study is available from the lead contact.

Data and code availability

All data supporting the findings of this study are included in the manuscript and its supplemental information, or from the corresponding authors upon reasonable request.

This study did not generate any code.

Materials

Branched polyethyleneimine (bPEI, Mw = 25 kDa) was purchased from Sigma Aldrich. 1DLs were synthesized using a recently developed one-pot solution-based method detailed in the supporting information.

bPEI-1DL hybrids preparation

bPEI-1DL nanocomposite samples were prepared by mixing bPEI and 1DLs in deionized, DI, water at precalculated mass ratios. The 1DL suspension was bath-sonicated for 1 min and then further diluted to a concentration of 2 g/L (1DL to water) before being sonicated again for 1 min. A 2g/L b-PEI water solution was prepared and added into the above-mentioned 1DL suspension under vigorous stirring for 10 min using a stir bar. A series of mbPEI-1DL hybrids were obtained via solution casting of the mixed suspensions. A 3 mL mixture of bPEI-1DL was cast onto glass

slides precleaned with distilled isopropanol. All samples were dried under vacuum at 50-60°C for 12 h before characterizations.

Characterization

XRD patterns were acquired utilizing a powder diffractometer (Rigaku SmartLab) equipped with $\text{CuK}\alpha$ radiation operating in the Bragg-Brentano configuration. Scanning was performed over a 2θ range of $1 - 25^\circ$ for the hybrids and $1-70^\circ$ for neat 1DL. TGA scans were conducted using a thermal analysis system (Perkin Elmer TGA 7 Series) with a heating rate of $20^\circ\text{C min}^{-1}$ under a nitrogen atmosphere, spanning the 50°C to 600°C temperature range. PLM images were captured employing an optical microscope (Olympus BX51) coupled with a digital camera (Diagnostic Instruments SPOT Insight model 3.2.0).

SEM images were taken on a scanning electron microscope (Thermo Scientific Apreo 2S). The accelerating voltage was 20 KV, and the signal was captured by an in-lens BSE detector. To prepare a top-view sample, the sample suspension was drop-cast onto a pre-cleaned silicon wafer. For cross-sectional images, the composites were drop-cast on a glass slide, and the films were peeled off and broken to reveal cross-sections of dried samples. Broken films were mounted on a 90-degree sample stub for imaging. AFM images were obtained from a Bruker Multimode 8 AFM using the PeakForce Tapping mode. An antimony (n) doped Si cantilever with an eight nm tip radius with a 42N/m spring constant was used. Composite suspensions were spincoated onto a Si-wafer at a rate of 1000 rpm for 30 s for AFM imaging.

Supplemental information

Supplemental information can be found online at:

Acknowledgments

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Author contributions

C.Y.L. and M.W.B. conceived the idea and supervised the experimental work. T.Z., S.Y., and Y.W. synthesized and characterized the hybrids. M.A.I., A.D.W., and G.R.S. synthesized and characterized 1DL. Y.-J.H. conducted the DFT work. C.Y.L. supervised the project and wrote the manuscript. All authors discussed the results and commented on the manuscript.

Declaration of interests

M.W.B. has recently filed a number of patents on 1DL materials.

Main figures and schemes

Scheme 1. Arresting the 1D-2D transition in 1DLs via polymer wrapping. (A, B) Schematic representation of the 1D (A), and 2D (B) structures of 1DLs. The 1DLs grow along the a axis and stack in the b direction. (C) 1D to 2D evolution without (top), and with (bottom), polymer coating, highlighting that polymer coating arrests the 1D-2D transition. The red and blue spheres in the figure denote oxygen and titanium atoms, respectively.

Figure 1. Characterization of 1DL and bPEI-1DL structures. (A) XRD patterns of neat 1DL, 0.1bPEI-1DL, and 0.2bPEI-1DL. (B) XRD pattern of 0.5bPEI-1DL, suggesting a Col^{hex} structure. Inset shows a schematic of proposed Col^{hex} viewing along the 1DL nanofilament axis. (C) Electron density map of the 0.5bPEI-1DL Col^{hex} phase calculated from (B). (D) Electron density map

calculated from the neat 1DL XRD pattern in (A). (E, F) AFM height images of neat 1DLs and 0.5bPEI-1DLs. Height profiles suggest the thicknesses of the filaments is ~ 0.8 nm and 1.8 nm, respectively.

Figure 2. Tuning the spacing of the columnar hexagonal phase. (A) XRD patterns as a function of m varied from 0.5 to 1.5. (B) Schematics showing changes in inter-filament distances with increasing polymer content. (C-J) SEM images of films, (C-D), neat 1DL, (E-F) 0.1bPEI-1DL, (G-H), 0.5bPEI-1DL, and (I-J) 0.8bPEI-1DL.

Figure 3. Morphology and phases of mb PEI-1DL hybrids as a function of m . (A) PLM images, from left to right, of samples 0.1bPEI-1DL, 0.5bPEI-1DL, 1.5bPEI-1DL, and 5bPEI-1DL, respectively. Scale bars indicate 40 μ m. (B) XRD patterns of 5bPEI-1DL and 19bPEI-1DL. (C) Three phases observed in mb PEI-1DLs; blue, green and red regions representing 2D structures, Col^{hex} phases, and isotropic phases, respectively. The Y axis presents the inter-sheet distance in 2D materials (open circles) and d^{hex} in the Col^{hex} phase (filled circles).

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