Liquid crystals of neat boron nitride nanotubes and their assembly into ordered macroscopic materials

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Boron nitride nanotubes (BNNTs) have attracted attention for their predicted extraordinary properties; yet, challenges in synthesis and processing have stifled progress on macroscopic materials. Recent advances have led to the production of highly pure BNNTs. Here we report that neat BNNTs dissolve in chlorosulfonic acid (CSA) and form birefringent liquid crystal domains at concentrations above 170 ppmw. These tactoidal domains merge into millimeter-sized regions upon light sonication in capillaries. Cryogenic electron microscopy directly shows nematic alignment of BNNTs in solution. BNNT liquid crystals can be processed into aligned films and extruded into neat BNNT fibers. This study of nematic liquid crystals of BNNTs demonstrates their ability to form macroscopic materials to be used in high-performance applications.
boron nitride nanotubes (BNNTs) are high aspect ratio rod-like nanostructures a few nanometers in diameter and microns long. Chemically, BNNTs are composed of alternating boron and nitrogen atoms in a hexagonally-bonded sheet, scrolled to form a seamless cylindrical structure that gives rise to several unique properties. In addition to being mechanically strong, BNNTs are thermally conductive, electrically insulating, neutron-shielding, piezoelectric, and thermally stable up to 900 °C in air. These properties are desirable for many applications, including aerospace, electronics, and energy-efficient materials. However, the utility of BNNTs is not yet fully realized, because their remarkable properties have only been observed at the microscopic level. Future improvements in material quality and processing techniques will enable high-performance neat BNNT articles with extraordinary properties for use in extreme environments.

The inherent properties of nanoscale building blocks can be translated to the macroscopic scale by controlling long-range ordering, as has been achieved with carbon nanotubes (CNTs), structural analogs of BNNTs that share many of their desirable properties, apart from superior thermal stability. For example, closely packed and highly aligned CNT fibers yield high performance (e.g., tensile strength above 4 GPa and electrical conductivity above 10 MS/m) via multiple routes, including direct spinning, wet spinning, and carpet spinning.

Thus far, none of these methods has been effectively employed to produce ordered BNNT materials. Of these routes, wet spinning appears most easily adapted to processing BNNTs because it is independent of synthesis method. Yet, wet spinning requires a solvent for the nanotubes and preferably the formation of a nanorod liquid crystal. Dispersions of individualized BNNTs can be achieved using chlorosulfonic acid (CSA). Kleinerman et al. hypothesized that protonation of nitrogen atoms of the outer BNNT wall confers a net positive charge to their surface; positively charged BNNTs repel each other leading to their individualization, as is the case for CNTs. However, the bond structure of BNNTs would localize protons on the nitrogen atoms—unlike in CNTs, where shared π electrons favor delocalization and hence further stabilization of positive charges when CNTs are dissolved in acids. This less effective charge stabilization (and hence further stabilization of positive charges when CNTs are dissolved in CSA) is consistent with the higher-than-UV-visible and Fourier transform infrared (FTIR) spectroscopy indicate that dissolution in CSA does not chemically alter BNNTs (Supplementary Figs. 3 and 4). Cryogenic-TEM (Cryo-TEM) of low-concentration HP-BNNT solutions (Fig. 1f) shows individualized BNNTs in CSA. Cryo-TEM also reveals that trace contaminants in HP-BNNTs (black and white arrows) envelop short segments of individual BNNTs. HP-BNNT diameter and length are characterized by AFM (Supplementary Fig. 5a–d), diameter and number of walls by TEM (Supplementary Fig. 5e–g), and aspect ratio via capillary thinning extensional rheometry. The results summarized in Table 1 show that all the techniques yield consistent results (within measurement error), with a typical aspect ratio of ~300 for HP-BNNT. Polarized light microscopy (PLM) images of BNNT solutions in sealed capillaries reveal important information about the solution quality such as degree of dissolution and anisotropy. LP-BNNTs at 7000 ppm by weight (ppmw) (Fig. 2a) have a gel-like behavior and show little birefringence, indicating no molecular orientational ordering, likely because BNNTs are trapped in the h-BN-induced network visible in Fig. 1a, c. Conversely, solutions of HP-BNNTs (Fig. 2b) display a brightly birefringent Schlieren texture, a hallmark of nematic liquid crystals. The presence of areas that remain dark for all crossed-polarizer angles (red arrows) suggests that the solution is biphasic (isotropic-nematic). Brief bath sonication of these filled capillaries promotes the merging of the nematic regions into larger domains that span the 1 mm width of the capillary (Fig. 2c).

Results and discussion

We synthesize the BNNTs via the high-temperature-pressure method (HTP) and purify them to remove residual elemental boron, producing "lightly processed" BNNTs (LP-BNNTs). LP-BNNTs are further purified to remove non-nanotube BN, producing "highly processed" BNNTs (HP-BNNTs)—see "Methods". Thermogravimetric analysis (TGA) of LP-BNNTs and HP-BNNTs in air (Supplementary Fig. 1) shows no mass gain from oxidation below 900 °C, indicating the absence of elemental boron impurities. The 35% mass increase at 1100 °C due to the oxidation of boron nitride is consistent with TGA from previous reports of pristine BNNTs. Because TGA does not distinguish between the oxidation of BNNTs and other boron nitride allotropes, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to assess relative BNNT purity. Figure 1a, c shows that LP-BNNTs samples contain agglomerates of h-BN (white arrows) that envelop overlapping BNNT bundles to create an apparent crosslinked BNNT network. The HP-BNNT samples (Fig. 1b, d) have a lower concentration of smaller h-BN aggregates (white arrows). TEM shown in Fig. 1d reveals that the few remaining non-nanotube structures in HP-BNNTs are few-layer stacks of h-BN. Consistent with literature values, the h-BN stack exhibits an interlayer spacing of 0.337 nm (Supplementary Fig. 2), determined by selected area fast Fourier transform.

Purified BNNTs spontaneously dissolve in CSA upon high-shear mixing to form homogenous liquids. LP-BNNTs in CSA (Fig. 1e, right) appear white and opaque, likely from scattering of micron sized aggregates of h-BN and BNNTs (visible in Fig. 1a, c) that do not dissolve well. Conversely, HP-BNNT solutions (Fig. 1e, left) typically have a peach color and are more transparent to the eye at the same concentration due to reduced optical scattering from individualization, owing to a superior purity.

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sonication. Likely, sonication provides enough energy to overcome the kinetic barriers that prevent the merging of tactoids. Tactoids are observed in solutions of HP-BNNTs at all studied concentrations, from 50 ppmw to 7260 ppmw (Supplementary Fig. 7c, d) so that BNNTs in tactoids persisting after dilution would fully disperse. Interestingly, the isotropic cloud point for these BNNTs was determined to be 170 ppmw (220 ppm by volume). This determination was made using images of capillary-sonicated solutions in Supplementary Fig. 7c, d so that BNNTs in tactoids persisting after dilution would fully disperse. Interestingly, the isotropic cloud point for these BNNTs is an order of magnitude lower than what would be expected for CNTs of similar aspect ratio29. This is consistent with less effective charge stabilization relative to CNTs, resulting in residual attraction and lowered isotropic cloud points, as observed in CNT solutions with decreasing acid strength23,33,34—in fact, extensional flow was recently used to form continuous macroscopic fibers of BNNT/polyvinyl alcohol35 by adapting the spinning technique originally developed for making CNT/PVA fibers16. We produce aligned BNNT films of HP-BNNTs by manually shearing a small aliquot of their solution in CSA between two glass slides. The shear forces align nematic domains along the shear direction. Coagulation in acetone immediately after shearing preserves the ordered structure by quickly removing CSA from the BNNTs, which adhere to the glass slide. Fully coagulated films can be lifted from the glass slide and floated on the surface of a bath of water (Fig. 3a). The films can then be redeposited onto other structures, such as another glass slide (Fig. 3b). These thin BNNT films are highly transparent to visible light, uniform, and free of haze, as displayed by the sharp image of the Rice University shield below the film (Fig. 3c). PLM of these films (Fig. 3d) shows a dark field of view for crossed-polarizer orientations of 0°/90° and bright field of view for a 45°/135°, indicating BNNT alignment along the direction of shear (0°). The periodic birefringence intensity and absorbance can be fit to classical equation forms for anisotropic solutions prior to loading into capillaries can in some cases break up tactoid domains while retaining the Schlieren texture observed in Fig. 2b. Although the impurities in LP-BNNTs solutions inhibit BNNT dissolution and the formation of tactoids, capillary sonication results in the same long-range alignment as in HP-BNNT solutions, but with a significant quantity of undispersed particles present (Supplementary Fig. 8).

The spontaneous alignment of BNNTs in liquid crystalline solutions is advantageous for the assembly of these building blocks into ordered macroscopic materials. Here, we are using lower concentration biphasic solutions in order to obtain processable volumes with the amount of HP-BNNT material available at this time. The lack of a fully liquid crystalline solution does not preclude the possibility of producing solid BNNT assemblies, because controlled flow induces alignment, even in an isotropic solution of rigid rods33—in fact, extensional flow was recently used to form continuous macroscopic fibers of BNNT/polyvinyl alcohol35 by adapting the spinning technique originally developed for making CNT/PVA fibers16. We produce aligned BNNT films of HP-BNNTs by manually shearing a small aliquot of their solution in CSA between two glass slides. The shear forces align nematic domains along the shear direction. Coagulation in acetone immediately after shearing preserves the ordered structure by quickly removing CSA from the BNNTs, which adhere to the glass slide. Fully coagulated films can be lifted from the glass slide and floated on the surface of a bath of water (Fig. 3a). The films can then be redeposited onto other structures, such as another glass slide (Fig. 3b). These thin BNNT films are highly transparent to visible light, uniform, and free of haze, as displayed by the sharp image of the Rice University shield below the film (Fig. 3c). PLM of these films (Fig. 3d) shows a dark field of view for crossed-polarizer orientations of 0°/90° and bright field of view for a 45°/135°, indicating BNNT alignment along the direction of shear (0°). The periodic birefringence intensity and absorbance can be fit to classical equation forms for anisotropic

### Table 1 Summary of bootstrapped HP-BNNT statistics.

| Aspect ratio (L/D) | Rheometry/TEM | AFM |
|-------------------|---------------|-----|
| Diameter (nm)     | 5.8 ± 0.3     | 5.6 ± 0.2 |
| Length (μm)       | 1.65 ± 0.29   | 1.54 ± 0.06 |
| Aspect ratio (L/D) | 257 ± 46      | 294 ± 14  |
films, $\sin^2(\theta)\cos^2(\theta)$ and $\sin^2(\theta)$, respectively. Good fits to the expected birefringence and absorbance indicate that the HP-BNNT film is aligned along the shear direction—although absorbance differences are minimal, because the visible light absorbance of BNNTs is low both for parallel and perpendicular orientations between the BNNT and the light polarization. The reduced birefringence intensities at 135° and 315° are likely due to a twist in the nematic director of the film. The dichroic ratio, determined from the birefringence intensity in Fig. 3e, can be used to estimate the film order parameter $S_{bir} = 0.56$. Alignment of BNNT bundles can be observed by SEM, which shows mild alignment along the shear direction on the top layer of BNNTs (Fig. 3f).

Liquid crystals are ideal precursors for aligned BNNT fibers. We produce fibers of neat HP-BNNTs via wet solution spinning, similar to other acid solution spinning processes. The ~1 wt% HP-BNNT solution, or dope, is extruded vertically from a syringe through a 150 μm spinneret into acetone. Acetone coagulates the extruding filament into a solid fiber by extracting and reacting with CSA (Fig. 4a). Figure 4b shows SEM of typical fibers, with an average diameter of 27 μm ± 1 μm variation along the fiber length. Higher magnifications in SEM reveal a wrinkled skin with mild axial alignment of BNNTs along most of the fiber. The uneven surface morphology is likely a result of collapse induced by rapid evaporation of the coagulant from the BNNT filament after removal from the coagulant bath with no applied draw during extrusion. Closer inspection of the surface wrinkles shows BNNT alignment along their contours (Fig. 4c). Elsewhere are isolated domains of highly aligned BNNTs oriented along the fiber axis (Fig. 4d). Wide-angle X-ray scattering (Fig. 4e) of typical BNNT fibers shows axial alignment. The full-width-half-max (FWHM) of 42° indicates that the BNNT fiber has somewhat higher alignment than early CNT fibers, which had a FWHM of ~60°. Polarized Raman spectra of that same BNNT fiber show a strong peak of BNNT at around 1370 cm$^{-1}$ (Fig. 4f), which corresponds to the transverse optical A1 vibrational mode. The intensity of the 1370 cm$^{-1}$ band is shown to be polarization-dependent, which is consistent with BNNT alignment. Figure 4f shows that the maximum intensity of the characteristic peak at 1370 cm$^{-1}$ is under the parallel polarization modes (V0° and V180°) and the...
minimum is under the perpendicular polarization (V90°) mode, suggesting a two-fold symmetry. The peak intensity ratio of V0°:V90° is estimated as 2.4:1, consistent with mild BNNT alignment along the fiber axis. This ratio is somewhat lower than the Raman peak ratio of 5.1:1 observed in early CNT fiber. The strongest BNNT fibers show an average (over twelve measurements) tensile strength of 15.7 MPa ± 1.6 MPa and Young’s modulus of 1.46 GPa ± 0.18 GPa, based on a diameter of 27 μm and circular cross-section. The BNNT fiber properties reported here are encouraging, given the similarities between BNNTs and CNTs. In fact, these initial results are comparable to those of early solution-spun HiPco CNT fiber, which had a strength of ~1 to 5 MPa and modulus of ~0.1 to 1 GPa (see Chapter 3 of ref. 44). The performance of early HiPco CNT fiber was limited by material impurity, but was later improved by two orders of magnitude by optimizing HiPco material processing. Later, CNT fiber performance was further improved by a factor of ~50 by combined advances in CNT quality and spinning.

In conclusion, we have shown that purified few-walled BNNTs are soluble in CSA and can be processed into macroscopic materials. BNNTs form nematic liquid crystals in CSA, including tactoids in biphasic solutions at the concentrations we tested (~1 wt%). We measured the aspect ratio of BNNTs and modulus of ~0.1 to 1 GPa (see Chapter 3 of ref. 44). The performance of early HiPco CNT fiber was limited by material impurity, but was later improved by two orders of magnitude by optimizing HiPco material processing. Later, CNT fiber performance was further improved by a factor of ~50 by combined advances in CNT quality and spinning.

Fig. 3 Aligned films of BNNTs. a Photograph of a BNNT film made from a ~1 wt% solution of highly purified BNNTs (HP-BNNTs) floating on water with its original structure intact. b Photograph of the same film as in a redeposited onto a new glass slide and held at an angle to observe the film more easily. c Photograph of the BNNT film from b on the glass slide laid over the Rice shield, demonstrating high transparency. d Polarized light microscopy (PLM) images of the BNNT film on a glass slide: unpolarized transmitted light image and polarized light images with polarizer/analyzer at fixed at 0°/90°. The film was rotated to 45° for the last polarized light image and the double-sided white arrows in the lower left corners of the PLM images indicate the orientation of the shear axis for the film. e Plot of HP-BNNT film birefringence intensity normalized by incident light intensity (circles) and film absorbance (squares) against stage rotation angle. Birefringence intensity and absorbance are both plotted with model fits with coefficients of determination (r²) of 0.996 and 0.991, respectively. f Scanning electron micrograph of the BNNT film on glass. The double-sided white arrow indicates the shear axis for the film on SEM micrograph.
quality, and processing parameters. Further improvements in material synthesis, purification, and mapping of the liquid crystalline phase diagram will yield optimal processing dopes. The nematic transition for solutions of CNTs has been observed through rheological characterization of CNT-supracritical solutions, and such experiments could help identify this transition for BNNT solutions. Fully liquid crystalline, higher concentration dopes will be explored in future experiments as HP-BNNTs become more broadly available. Such improved dopes will allow spinning in a broader parameter space with stable properties in extreme environments.

Methods

Synthesis and purification of BNNTs. BNNTs for this research were synthesized by BNNT LLC (Newport News, VA), using the HTP method. The as-synthesized samples (product code SP10) were then purified to remove elemental boron, yielding LP-BNNTs (product code SP10R). LP-BNNTs include non-nanotube boron nitride species, which can be removed by high-temperature steam purification. LP-BNNTs were further purified by a high-temperature steam purification process to remove non-nanotube BN species, yielding HP-BNNTs (product code SP10RX). TGA was performed using a Mettler Toledo TGA/DSC 1 in air with a 10-min hold at 110 °C and a temperature ramp of 10 °C/min to 1100 °C for all samples.

Solution preparation and spectroscopy. The BNNTs were dissolved in CSA at a concentration of ~1% by weight. Pure (99.9%) CSA was used as received from Sigma-Aldrich. The vial containing BNNTs and CSA was first vigorously shaken by hand to break apart the BNNT “puff ball,” prior to mixing for 40 min with a FlackTek DAC 600 SpeedMixer forming a viscous solution. UV–vis spectra of the BNNTs dissolved in CSA and dispersed in 1% by weight aqueous sodium dodecyl sulfate (SDS) were collected using a Shimadzu UV-1800 spectrophotometer. Quartz cuvettes with PTFE caps and path lengths of 1 mm and 1 cm were used for UV–vis and FTIR spectroscopy, respectively. BNNT solutions in CSA were quenched and rinsed with deionized water until a neutral pH was reached. The BNNTs were then dried to collect FTIR spectra. A Nicolet iS5 instrument was used with a diamond ATR accessory, averaging 32 scans at 4 cm⁻¹ resolution.

Rheology and aspect ratio determination of BNNTs. Viscosity-averaged aspect ratios were estimated using a custom-built capillary thinning rheometer, described by ref. The extensional viscosity is determined by the rate-of-change of the filament diameter. Supplementary Fig. 6 shows the final frames of filament thinning that were recorded during the experiment. An extensional viscosity of 0.4 Pa s was determined for the 7260 ppmw solution. A density of 1.50 g/cm³ was used for the HP-BNNTs to calculate the viscosity-averaged aspect ratio. This density was calculated assuming that a single-walled BNNT has the same areal density as a single sheet of h-BN (1318 m²/g), following along with similar calculations for graphene. The density of HP-BNNTs was calculated using the average number of walls (3.3) and outer diameter (5.8 nm ± 0.3 nm), while also assuming with a BN bond length of 1.466 Å, and an interlayer spacing of 3.33 Å (refs. 28,49).

BNNT films and fibers. Shear-aligned films were produced according to the method described by ref. 30, using acetonitrile as the coagulant. Just prior to shearing the solution, a powered 20 kHz Qsonica Q55 tip sonicator was lightly brushed along the outer surface of the top glass, scratching the glass and merging tactoid domains. The top slide was then rapidly sheared across the bottom slide and immediately plunged into an acetonitrile coagulant bath. Shear-aligned films were annealed in air at 400 °C for 20 min to improve electron imaging quality by removing residual acid and organic molecules from coagulation. BNNT fibers were produced by extruding BNNT solution through a 150 μm spinneret into a coagulation bath of acetonitrile, based on methods described by ref. 31. Fiber was extracted from the bath and allowed to dry under ambient conditions overnight, before tensile testing on an ARES-G2 rheometer, using 4 mm fiber segments.

Light microscopy. Portions of HP-BNNT and LP-BNNT CSA solutions were loaded and flame-sealed into glass capillaries with an inner width of 100 μm, which were then flame-sealed. Some sealed capillaries were sonicated by submerging them into a Branson 1800 bath sonicator at 40 kHz for ~5 s. Light microscopy was performed with a Zeiss Axioplan 2 microscope equipped with a Zeiss AxioCam 208 1.6 MP camera. The contrast for images of sealed capillaries was adjusted in MatLab and ImageJ. Each set of PLM images received the same contrast adjustments. Images of the BNNT film that were used to study birefringence and absorption were taken...
with the camera operating in black-and-white mode without contrast adjustments. Intensities for each rotation angle were determined by averaging the pixel values across the entire field of view (~1 mm × 0.65 mm). The incident light intensity was determined by capturing an image with no sample and only the polarizer inserted. All images for this analysis were taken using the same microscope illumination settings and intensity values were normalized by camera exposure time.

**Atomic force microscopy.** Samples for atomic force microscopy (AFM) were prepared from solutions diluted to ~1 ppmw and drop-cast onto a freshly cleaved mica surface, preheated to 400 °C using a hot plate. Diethyl ether was used to remove residual acid from the mica before drying the sample with room temperature air flow, followed by oven treatment at 100 °C for an hour. The AFM measurements were performed with a Nanoscope IIIa scanning probe microscope controller from Digital Instruments operated in the tapping mode. Micrographs were processed in the Gwyddion software package, and the height profiles and length of 100 randomly selected individual nanotubes were collected.

**Electron microscopy.** SEM of dry material was performed using an FEI Helios NanoLab 660 SEM/FIB. Shear-aligned films were imaged directly on glass, and the as-produced material was imaged on carbon tape. SEM samples received no conductive layer prior to imaging. An accelerating voltage of ~1 kV and working distance of ~3.5 mm was used for SEM characterization.

TEM and Cryo-TEM of BNNT-CSA solutions were performed by a Thermo Fisher (formerly FEI) Talos 200C high-resolution TEM at an accelerating voltage of 200 kV. Cryo-samples were maintained below 175 °C in the microscope using a Gatan 626 cryo-holder, and imaged in the low-dose-imaging mode to reduce electron-beam radiation damage. Images were recorded digitally by an FEI Falcon III direct-imaging camera and the TIA software, with the help of the "Volta phase-plate" (FEI) to enhance image contrast.

Cryo-TEM of BNNT-CSA solutions was performed by a Zeiss Ultra Plus HR-SEM equipped with a Leica VT100 cold-stage system. Specimens were maintained at ~145 °C and without coating at a low acceleration voltage of 0.6 kV to achieve a state of charge balance, avoiding specimen charging and imaging artifacts. Micrographs were taken at short working distance (3.3–3.8 mm) with an in-column secondary electron detector. Cryo-TEM and cryo-SEM specimens were prepared in a controlled environment vitrification system, continuously purged with dry N₂ to prevent superacid reaction with moisture. Cryo-TEM specimens, a drop was applied onto a perforated carbon film supported on a 3 mm copper TEM grid. The drop was blotted with a fiberglass filter-paper to form a thin film (<300 nm) and vitrified by plunging into liquid nitrogen. Cryo-SEM specimens were prepared by dipping a 3 mm grid in the solution and placing it between two gold planchets. The specimen was plunged into liquid nitrogen with dedicated tweezers, and freeze-fractured in a BA9060 unit (Leica AG, Liechtenstein) at ~167 °C.

**Raman spectroscopy.** Raman spectra were obtained with a DXR2 Raman microscope system (Thermo Fisher Scientific) equipped with a laser excitation of 785 nm under ×50 objective. The BNNT fiber samples were placed onto a glass slide, and analyzed within the Raman shift range of 200–3400 cm⁻¹. The Raman microscope was operated with the following experimental parameters: excitation wavelength (785 nm), laser intensity (30 mW), and aperture type (50 µm). The spectral background was corrected using smart subtraction offered by the DXR2 Raman microscope to remove interference caused by fluorescence. The alignment of the BNNT fiber was determined by recording a Raman spectrum every 30° from 0° to 180° in between the incident polarization and the fiber axis. While the polarizer was set vertically, Raman spectra were collected from BNNT fiber in the order of V° (parallel polarization), V90°, V60°, V90° (perpendicular polarization), V120°, V150°, and V180° analyzer modes.

**Data availability**

The main data that support the findings of this study are available in the article and Supplementary Information. Raw data are available from the corresponding author upon reasonable request.

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Supplementary Information for

**Liquid Crystals of Neat Boron Nitride Nanotubes and their Assembly into Ordered Macroscopic Materials**

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Thermogravimetric analysis (TGA) of LP-BNNTs and HP-BNNTs in Supplementary Fig. 1 shows no residual boron after the two respective purifications. UV-vis spectroscopy of CSA solutions of HP-BNNTs and LP-BNNTs are shown in Supplementary Figs. 3a and 3b. Extinction coefficients at 350 nm (Supplementary Fig. 3c) are determined to be $9.87 \times 10^{-3}$ mL·µg$^{-1}$·cm$^{-1}$ for LP-BNNTs and $3.68 \times 10^{-3}$ mL·µg$^{-1}$·cm$^{-1}$ for HP-BNNTs. The larger extinction coefficient for LP-BNNTs quantifies the higher degree of scattering. These extinction coefficients can be used to determine solution concentrations. UV-vis spectra of recovered (previously dissolved in CSA) HP-BNNTs and LP-BNNTs in 1 wt% aqueous sodium dodecyl sulfate (SDS) solutions show maximum absorbances at 204 nm. The Tauc plot in Supplementary Fig. 3d is used to determine optical band gaps for HP-BNNTs and LP-BNNTs of 5.79 eV and 5.67 eV, respectively, which are consistent with the theoretical value of 5.5 eV (ref. 1). The slightly higher band gap of HP-BNNTs relative to LP-BNNTs is consistent with band gap measurements of individual BNNTs and h-BN particles by electron energy loss spectroscopy (EELS), possibly indicating that the value reported here is sensitive to the degree of h-BN contamination. FTIR spectroscopy of recovered HP-BNNTs and LP-BNNTs (Supplementary Fig. 4) shows the B-N bending mode at 802 cm$^{-1}$ and B-N stretching at 1350 cm$^{-1}$ (ref. 3), indicating that the chemical nature of BNNTs is maintained, even after purification, dispersion, quenching, and recovery from CSA.

TEM images of 106 BNNTs are analyzed for diameters and number of walls. The outer BNNT diameter by TEM is paired with aspect ratio measurements from extensional rheometry to determine length, and the number of walls is used to determine the mass density. Atomic force microscopy (AFM) images of 100 BNNTs are analyzed for BNNT diameters and lengths (Supplementary Fig. 5) as an independent measure of BNNT aspect ratio to validate the combined TEM and rheometry results. TEM and AFM data are resampled with replacement according to the
bootstrap method to determine more accurate estimates of variance for these data. The bootstrapped variable statistics approach the population statistic values in the limit of an infinite number of resampling, assuming that the sample is an unbiased representation of the population\textsuperscript{4,5}. The size of each resampled group, $n$, was equal to the size of the parent data set, $N$, and each data set was sampled $10^6$ times.

HP-BNNT solutions are characterized via capillary thinning extensional rheometry (Supplementary Fig. 6), in which a liquid bridge of BNNT solution placed between two pistons is suddenly stretched in front of a high-speed camera. The rate of decrease of the liquid filament diameter is used to determine an extensional viscosity of the solution, which can be used to estimate the aspect ratio of rod-like nanoparticles\textsuperscript{6}. HP-BNNT solutions behave as homogeneous liquids, similar to solutions of CNTs in CSA\textsuperscript{7}. 
Supplementary Fig. 1 Thermogravimetric analysis (TGA). TGA of lightly purified BNNTs (LP-BNNTs) and highly purified (HP-BNNTs) was performed in dry air at 10 °C/min to 1100 °C with a 10-minute hold at 110 °C to ensure samples were dry.
Supplementary Fig. 2 HP-BNNT impurities. a Transmission electron microscopy of a hexagonal boron nitride (h-BN) particle adhered to highly purified BNNTs with selected area outlined in red. b Selected area fast Fourier transform indicating an inter-layer spacing 0.337 nm. The few h-BN impurities that remain do not couple BNNTs together, but could negatively impact BNNT alignment and packing density.
Supplementary Fig. 3 UV-visible spectroscopy (UV-vis). a UV-vis absorbance spectra of lightly purified BNNTs (LP-BNNTs) in chlorosulfonic acid (CSA) at various concentrations measured with a 1 mm path length. b UV-vis absorbance spectra of highly purified BNNTs (HP-BNNTs) in CSA at various concentrations measured with a 1 mm path length. The absorbance cutoff for CSA (A = 1 a.u.) was measured to be 259 nm using a 1 cm path length cuvettes with water in the reference cell. c Linear fits to the absorbances of LP-BNNTs and HP-BNNTs at 350 nm used determine extinction coefficients of $9.87 \times 10^{-3}$ mL·μg$^{-1}$·cm$^{-1}$ and $3.68 \times 10^{-3}$ mL·μg$^{-1}$·cm$^{-1}$, respectively. d Tauc plot of recovered (previously dissolved in CSA) LP-BNNTs and HP-BNNTs in 1 wt% aqueous SDS at 4 ppmw and 2 ppmw, respectively.
Supplementary Fig. 4 Fourier transform infrared spectroscopy (FTIR). FTIR spectra of as produced and recovered (previously exposed to CSA) BNNTs. Spectra are normalized to the intensity of the peak at 1350 cm$^{-1}$. 
Supplementary Fig. 5 Number of walls, length, diameter distributions. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) of BNNTs are used to determine BNNT properties for use in conjunction with capillary extensional rheology. 

**a** Typical AFM image on mica with inset line scan. 

**b** AFM diameter distribution for highly purified BNNTs (HP-BNNTs). 

**c** AFM length distribution for HP-BNNTs. 

**d** AFM aspect ratio distribution for HP-BNNTs. 

**E** Typical TEM image for HP-BNNTs. 

**f** TEM diameter distribution for HP-BNNTs. 

**g** TEM number of walls distribution for HP-BNNTs. 

**h** TEM diameter distribution for lightly purified BNNTs (LP-BNNTs). 

**i** TEM number of wall distribution for LP-BNNTs. LP-BNNTs have slightly smaller average diameter (5.4 nm ± 0.3 nm) and number of walls (3.4 ± 0.2), which may be a result of purification etching the outer walls of multi-walled BNNTs. The average diameters for both HP-BNNT and LP-BNNT agree within measurement error.
**Supplementary Fig. 6 Capillary thinning rheometry.** a Frames of a representative high speed video (1000 fps) during capillary thinning rheometry of a solution of highly purified BNNTs (HP-BNNTs) at 7260 ppmw in chlorosulfonic acid (CSA). b Plot of filament diameter. Sequence of frames is left to right, starting from the top row. The parameters for aspect ratio determination from capillary thinning rheology analysis are based off the following average property values from microscopic characterization: number of walls = 3.5; diameter = 5.8 nm; BNNT density = 1.50 g/cm$^3$. 
Supplementary Fig. 7 Tactoid persistence and isotropic cloud point transition. Polarized light microscopy (PLM) of highly purified BNNTs (HP-BNNTs) in chlorosulfonic acid (CSA) in flame-sealed 1 mm × 0.1 mm rectangular capillaries: unpolarized transmitted light and polarized light images with polarizer/analyzer at 0°/90° and 45°/135°, as depicted by the white crossed arrows. a Solution of HP-BNNTs in CSA at 7260 ppmw with no capillary sonication, showing the presence of tactoids (white arrows). b Solution of HP-BNNTs in CSA at 50 ppmw with no sonication, showing the presence of tactoids (white arrows). c Solution of HP-BNNTs in CSA at 250 ppmw showing faint birefringence in the lower half of the field of view. d Solution of HP-BNNTs in CSA at 90 ppmw showing no birefringence for the whole field of view. The isotropic cloud point is determined as the midpoint between these two concentrations, 170 ppmw (220 ppmv).
Supplementary Fig. 8 Induced nematic alignment in lightly purified BNNT (LP-BNNT) solutions. Polarized light microscopy (PLM) of lightly purified BNNTs (LP-BNNTs) in chlorosulfonic acid (CSA) (same as Fig. 2a) in flame-sealed 1 mm × 0.1 mm rectangular capillaries: unpolarized transmitted light and polarized light images with polarizer/analyzer at 0°/90° and 45°/135°, as depicted by the white crossed arrows. a 7000 ppmw solution of LP-BNNTs in chlorosulfonic acid (CSA) before capillary sonication appears isotropic because of low-intensity birefringence. b The same solution after capillary sonication showing birefringent nematic domains spanning the width of the capillary. Undissolved aggregates are present throughout the field of view.
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