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Purification and Assembly of DNA-Stabilized Boron Nitride Nanotubes into Aligned Films

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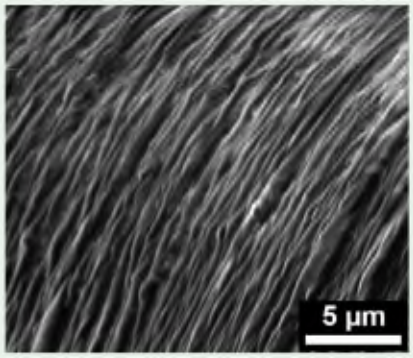
Supporting Information

ABSTRACT: The liquid phase processing including dispersion, purification, and assembly of boron nitride nanotubes (BNNTs) is important for effectively translating unique properties of BNNTs into assembled solid materials, such as films and fibers. Short single-stranded DNA (ssDNA) has been the biopolymer of choice to achieve efficient sorting and assembly of carbon nanotubes, which are structural analogues to BNNTs. Here, we demonstrated a highly efficient aqueous dispersion of BNNTs using $(GT)_{20}$ ssDNA and the subsequent removal of non-nanotube impurities from dispersions of as-synthesized BNNT material by a membrane filtration approach. The surface coating of BNNTs by DNA creates uniform dispersions at a nanotube concentration of as high as ≈11.5 mass %, leading to the formation of solid aligned films after solvent evaporation without applied shear, therefore demonstrating the first example of BNNT films produced by spontaneous alignment of nanotubes. Our findings provide important insights for producing macroscopic assemblies of aligned BNNT films for potential applications in thermal interface material and electronic and optoelectronic devices.



KEYWORDS: *boron nitride nanotubes, single-stranded DNA, nanotube dispersion, purification, aligned films*

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INTRODUCTION

Boron nitride nanotubes (BNNTs) have promising optical,[1] mechanical,[2] and thermal properties[3] for developing thermal interface material and electronic and optoelectronic applications.[4−6] Recent advances in high-throughput synthesis of BNNTs have led to a growing effort in scalable processing solution for making macroscopic assemblies of BNNTs.[7−9] The one-dimensionality and symmetry restrictions in high-aspect-ratio BNNTs, resembling that of carbon nanotubes, render new structural characteristics and unique properties that are not available in many existing nanomaterials.[10] Compared to electronic structures of single-wall carbon nanotubes (SWCNTs), which can be metals, quasi-metals, or semiconductors,[11] BNNTs with diameters larger than 1.2 nm behave as wide bandgap semiconductors independent of wall number and chirality.[12] In addition, BNNTs are stable under air oxidation up to 900 °C[3] and have optical absorbance and fluorescence features in the ultraviolet range.[13] These distinct properties make BNNTs one of the most promising material candidate for producing multifunctional, protective films with remarkable thermal and chemical stabilities and ultraviolet radiation shielding.[10]

The effective translation of unique properties of individual BNNTs into macroscopic assemblies requires a starting material with well-defined properties. Current scalable synthesis of BNNTs via a high-temperature-pressure (HTP) process[6,14] typically produces a mixture of few-wall BNNTs and large percentages of non-nanotube impurities, such as elemental boron, boron oxide (B_2O_3), and hexagonal boron nitride (*h*-BN) structures such as nanosheets and nanoshells.[15] The postsynthesis purification of BNNTs has been previously performed using acid and heat treatments; however, those techniques are mainly focused on the selective removal of elemental boron.[14] The alignment of nanotubes is also considered as an important factor to obtain assembled solid materials with improved properties, which has been demonstrated extensively for aligned films and fibers produced from carbon nanotubes.[16] To purify and align BNNTs through liquid phase processing as demonstrated in this work, a prerequisite is to obtain nanotubes in an individually dispersed state in a liquid medium.

To date, various surfactants,[17,18] aromatic molecules,[19] biomolecules,[20] including DNA,[13] and other polymers[21] have been utilized to disperse BNNTs through noncovalent complexation in an aqueous environment. BNNTs that are noncovalently complexed with single-stranded DNA (DNA-BNNTs) are of particular interest. Single-stranded DNA (ssDNA) has emerged as a sequence-controlled biopolymer of choice to effectively sort chirality-defined SWCNTs[22] and enable controlled assembly and technological applications of

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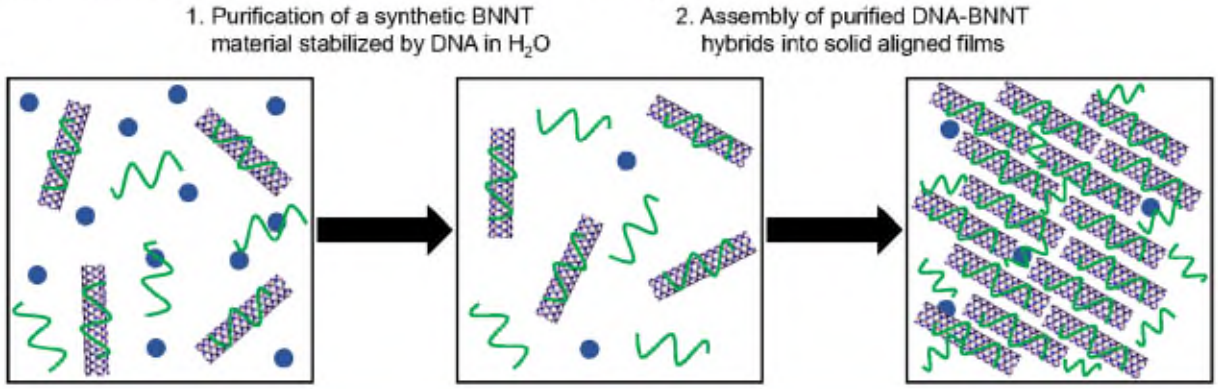
Scheme 1. Purification and Assembly Processes of DNA-BNNT Hybrids



SWCNTs with enhanced biocompatibility.[23,24] The interactions of single-wall BNNTs and short ssDNA revealed theoretically the wrapping conformation of DNA on the BNNT, resembling that of a DNA-SWCNT hybrid, via $\pi-\pi$ stacking of hydrophobic DNA nucleotide bases and the hydrophobic surface of an aromatic BNNT.[25] Furthermore, DNA-BNNT hybrids are stabilized by electrostatic interactions due to the charge-carrying phosphate−sugar DNA backbone that is exposed in the aqueous environment. The adsorption of DNA on BNNTs is dominated by the van der Waals interaction with a minor contribution from the electrostatic interaction as determined by the molecular dynamics simulation.[25] Notably, the ionic nature of the BN bond[10,12] and few-wall BNNTs[7] used in this study could lead to a drastically different DNA conformation on the surface of BNNTs. In addition, DNA-mediated assembly of a BNNT mat by membrane filtration was reported for multiwall BNNTs of an average diameter of ≈50 nm; however, a uniform dispersion at higher than ≈0.2 mass % BNNTs was not obtained due to nanotube aggregations.[13] Understanding the interactions of BNNTs and biopolymer DNA is essential to explore other biomolecules and polymers to better manipulate BNNTs in future work.

Here, we report a systematic study of aqueous dispersion, purification, and self-assembly of BNNTs using DNA. We demonstrated a highly efficient, aqueous dispersion of BNNTs using $(GT)_{20}$ ssDNA and the subsequent removal of non-nanotube impurities from aqueous dispersions of as-synthesized material by a membrane filtration approach. Furthermore, aqueous dispersions of purified DNA-BNNTs remained uniform at a nanotube concentration of as high as ≈11.5 mass %, which resulted in aligned BNNT films after solvent evaporation.

■ EXPERIMENTAL SECTION

Stock DNA-BNNT dispersions were prepared at various BNNTs/DNA mass ratios according to a standard procedure, which was previously developed for processing SWCNTs (see the Supporting Information).[22] The BNNTs/DNA mass ratio was varied from BNNTs:DNA = 1:0 up to 1:6 while keeping the concentration of as-synthesized BNNT mixture material constant at 1 mg/mL. Briefly, a synthetic BNNT material (Puff Ball, lot no. 44171, BNNT LLC) was dispersed in aqueous DNA (Integrated DNA Technologies) solutions containing 0.1 mol/L NaCl (Sigma-Aldrich) by sonication. Supernatants were collected after centrifugation and used as stock DNA-BNNT dispersions. The purification of BNNTs from non-nanotube structures remaining in the stock dispersion was performed via a membrane filtration method using a Microcon centrifugal filter with a molecular weight cutoff (MWCO) of 30 kDa. The retentate after membrane filtration was washed with deionized (DI) water three times before redispersing in water. An additional amount of DNA was added to a final concentration of 0.1 mg/mL to maintain the dispersion stability of purified DNA-BNNTs at higher concentrations of nanotubes. This yields a mass ratio of free DNA:DNA-BNNT hybrids ≈1.1:1 in the dispersion. Purified DNA-BNNT dispersions were further concentrated by evaporating the solvent at room temperature. The aligned BNNT film was obtained by drying ≈11.5 mass % DNA-BNNT dispersion on a plasma-treated silicon substrate.

UV−vis absorbance measurements were performed on a Shimadzu UV-2600/Jasco V-760 spectrophotometer over the wavelength range 185−800 nm using a 10 mm path length quartz cuvette. Excess DNA not bound to BNNTs was removed from the sample by a precipitation method[26] previously reported for carbon nanotubes to allow for resolution of BNNT absorption features in the UV region. Specifically, final concentrations of 1 mol/L sodium thiocyanate (NaSCN, Sigma-Aldrich) and 6 mass % poly(ethylene glycol) (PEG, MW 6 kDa, Alfa Aesar) were added to the sample. The mixture was incubated overnight at 4 °C and then centrifuged at 17000g for 30 min. After centrifugation, the supernatant was removed, and the pellet was redispersed in water by bath sonication for 30 min.

A high-resolution field emission scanning electron microscope (SEM), Inspect F50 by FEI, equipped with an Everhart-Thornley detector with variable grid bias was used to characterize dispersed DNA-BNNT hybrids as well as aligned DNA-BNNT films. The gold-sputtered silicon wafer substrate was used to image dried samples of dilute dispersions of DNA-BNNTs. For the densely packed DNA-BNNT films a bare silicon substrate was used instead, which was plasma treated to promote uniform transfer of the films to the substrate. The sample was scribed to reveal the underside of the film. SEM imaging was performed at 5 kV.

■ RESULTS AND DISCUSSION

A systematic approach of processing BNNTs including dispersion, purification, and assembly into solid aligned films was achieved using short ssDNA as a highly efficient dispersant for stabilizing BNNTs in water (Scheme 1). DNA confers a number of advantages including the potential to stabilize nanotubes through $\pi-\pi$ interactions in various solvents such as water and alcohols,[27] assist large area assemblies of nanotubes,[28,29] and offer green chemistry and multifunctionality. We first examined the capability of DNA to disperse BNNTs individually in an aqueous environment based on its potential for $\pi-\pi$ interactions.[25] Initially, we compared the dispersion capability of short ssDNA including single nucleotide repeats and $(GT)_n$ sequences, where n = 3, 5, 10, 15, or 20 repeats (see the Supporting Information). We found that sequences composed of G/T nucleotides led to effective dispersions of BNNTs regardless of the length of $(GT)_n$ sequences used,

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indicating that the DNA length is not a determining factor for forming a stable DNA-BNNT hybrid within the range of DNA length tested. In fact, it has been previously proposed for a $(GT)_n$-SWCNT system that the binding strength of specific DNA sequences toward nanotubes is the primarily determinant of the hybrid stability rather than the DNA length used and the DNA surface coverage created on nanotubes.[30] Consequently, we selected $(GT)_{20}$ ssDNA, which is one of the best known recognition sequences to effectively disperse and purify SWCNTs due to its ability to fold onto a nanotube to form a stable DNA-wrapped SWCNT hybrid.[22] The folding conformation of $(GT)_{20}$ on BNNTs in this work could be different from that of DNA-SWCNTs due to the ionic BN bonding and few-wall structures of BNNTs. Nonetheless, stock dispersions of DNA-BNNTs obtained in this work are stable for more than 12 months for a routine storage condition at 4 °C. Future studies involving cost-effective dispersants such as natural DNA and other polymers could be beneficial for the scale-up of the liquid phase processing of BNNTs, although the interactions of those polymers with nanotubes and the hybrid stability could be drastically different from that of DNA-BNNT hybrids created in this work using sequence specific $(GT)_n$ ssDNA.

Figure 1A compares aqueous dispersions of DNA-BNNTs prepared by three different methods: BNNTs:DNA = 1:0 without adding DNA, a bulk dispersion of BNNTs:DNA = 1:1 without centrifugation, and a supernatant of BNNTs:DNA = 1:1 collected after centrifugation. All BNNTs/DNA ratios of various nanotube dispersions are reported in mass ratios. The uniform dispersion of BNNTs in an aqueous environment was obtained only with the assistance of DNA. The centrifugation step enabled the further removal of the majority of bundled BNNTs and certain impurities as indicated by overall decreases in absorption peaks of DNA-BNNT dispersions. Specifically, we observed three characteristic peaks at 190, 205, and 220 nm wavelengths in the UV region (Figure 1B). Our SEM analysis of a BNNT dispersion without DNA showed particles of 22 ± 8 nm in size, suggesting that the 190 nm peak is likely to correspond to non-nanotube impurities such as elemental boron (see the Supporting Information).[15] The absorption of a DNA-BNNT hybrid corresponds to the 205 nm peak, which is in good agreement with a band gap of ≈6 eV for BNNTs.[12] Here, the concentration of nanotubes after precipitation and resuspension of a supernatant dispersion of BNNTs:DNA = 1:1 in deionized (DI) water is determined to be ≈0.382 mg mL^{-1} using an extinction coefficient of 0.0926 L mg^{-1} cm^{-1} at 205 nm for a DNA-BNNT hybrid (see the Supporting Information). Similar to the interactions of DNA and graphene, the hydrophobic DNA nucleotide bases can be potentially noncovalently complexed with *h*-BN structures, which likely gave rise to an absorption peak at 220 nm.[31] In general, an absorbance spectrum of a bulk dispersion showed increased background and broader peaks compared to that of a supernatant dispersion (see the Supporting Information). Significant decreases in absorbance values were observed for supernatant dispersions of BNNTs:DNA = 1:1, indicating the removal of the majority of BNNT bundles and other impurities with centrifugation. Figure 1C shows the length distribution of DNA-BNNT hybrids from a supernatant BNNTs:DNA = 1:1 sample by SEM, and the number-average length of hybrids was estimated to be 268 ± 110 nm (see the Supporting Information). Highly localized shear during the ultrasonication process likely resulted in the cutting of as-synthesized

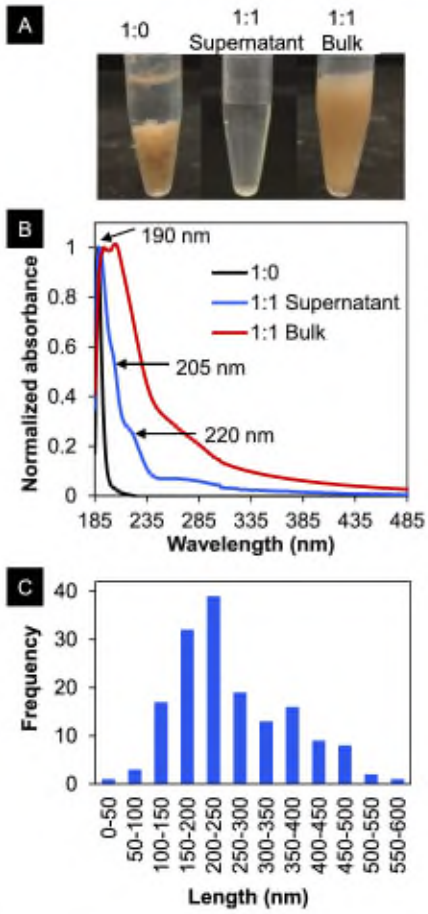

Figure 1. Aqueous dispersions of a synthetic BNNT material that are noncovalently complexed with $(GT)_{20}$ ssDNA. (A) Photographs of three different dispersions with BNNTs/DNA mass ratios of 1:0 and 1:1 before (i.e., bulk) and after (i.e., supernatant) centrifugation. (B) Corresponding absorbance spectra of DNA-BNNT dispersions. Arrows indicate characteristic absorption peaks at 190, 205, and 220 nm wavelengths. (C) Histogram of the length distribution of DNA-BNNT hybrids by measuring lengths of 200 nanotubes imaged by SEM.

nanotubes, which can be up to ≈200 μm long.[7] In addition, it has been reported recently that short $(GT)_{30}$-SWCNT hybrids bind preferentially to the imaging substrate (freshly cleaved mica) compared to long $(GT)_{30}$-SWCNTs due to their larger diffusion coefficients, resulting in a length distribution of nanotubes that is significantly smaller than the parent sample.[32] It could be possible that the length distribution of $(GT)_{20}$-BNNT hybrids determined in this work is smaller than the parent BNNT dispersion potentially due to the differential binding of hybrids to the silicon substrate. Although the accurate measurement of nanotube lengths and the production of long DNA-BNNT hybrids that are desirable for certain applications such as nanocomposites and fiber spinning can be rationalized by future studies, the ability to produce stable DNA-BNNT hybrids can nonetheless be exploited for purification and assembly of nanotubes, as shown in this work.

To determine the effective BNNTs/DNA mass ratio for dispersing as-synthesized BNNTs, we compared absorbance values of three characteristic peaks of supernatant dispersions with increasing concentrations of DNA (Figure 2A). The

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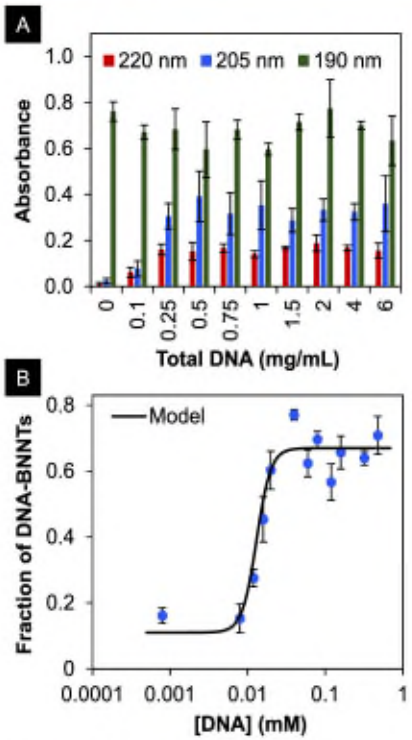

Figure 2. Dependence of $(GT)_{20}$-BNNT dispersion efficiency on the mass ratio of BNNTs/DNA. (A) Absorbance values of characteristic peaks observed at 190, 205, and 220 nm for supernatant dispersions of DNA-BNNTs at BNNTs/DNA mass ratios from 1:0 to 1:6. (B) Fraction of DNA-BNNT hybrids in supernatant dispersions as a function of DNA molar concentration. All samples were diluted by a factor of 100× in DI water for UV−vis absorbance measurements. The error bars were obtained from the standard deviation of a minimum of three repeats.

absorption of DNA-BNNT hybrids at 205 nm increased for dispersions roughly up to a BNNTs/DNA mass ratio of 1:0.5, indicating an improved dispersion yield of nanotubes, followed by a plateau with further increase in DNA concentrations. The overall trend of absorption at 220 nm for *h*-BN structures with increasing DNA concentrations was similar to that of DNA-BNNT hybrids, however, at lower absorbance values compared to that of DNA-BNNT hybrids (Figure 2A). It was reported previously that ssDNA can bind to flat graphite, however, at a much weaker binding strength compared to that of curved SWCNTs due to the spontaneous curvature of ssDNA.[31] Similarly, ssDNA is likely to stabilize *h*-BN impurities in a synthetic BNNT material through binding to the hydrophobic surface of *h-BN* structures. In addition, absorbance values of elemental boron at 190 nm remained relatively invariable at all BNNTs/DNA mass ratios tested, indicating that the dispersion yield of elemental boron is independent of the presence of DNA in an aqueous dispersion.

Our results show the fraction of DNA-stabilized BNNTs in an aqueous dispersion of synthetic BNNT mixture depended on the mass ratio of BNNTs/DNA. The change in absorbance values of a DNA-BNNT hybrid obtained in Figure 2A enables determining the fraction of nanotubes dispersed by DNA. The rapid increase in the fraction of DNA-BNNTs with increasing DNA concentration indicates that sufficient DNA molecules are needed to stabilize BNNTs in dispersions by overcoming strong van der Waals forces of attraction between nanotubes. However, the amount of DNA needed saturates at a certain point which is identified to be near 0.040 mM in this work. This corresponds to an initial dispersion of BNNTs:DNA = 1:0.5 mass ratio. The binding behavior of DNA on the sidewall of BNNTs in a stock DNA-BNNT dispersion can be described using a curve fitting approach of the Hill equation. Previously, the Hill equation arising from chemical kinetics was utilized to evaluate interactions of SWCNTs with biomolecules including DNA and dopamine.[33,34] Here, we treat it as an empirical equation to describe the interactions between nanotubes and DNA at equilibrium due to the structural polydispersity of the synthetic BNNT material. We consider the following equation to describe our system:

$$\text{DNA} + \text{BNNTs} \leftrightarrows \text{DNA-BNNTs} \tag{1}$$

The total concentration of BNNTs in a dispersion, $[\text{BNNTs}]_{tot}$, is the sum of the concentrations of bare BNNTs and nanotubes coated by DNA:

$$[\text{BNNTs}]_{tot} = [\text{BNNTs}] + [\text{DNA-BNNTs}] \tag{2}$$

We assume the fraction of the DNA-bound BNNTs in a supernatant dispersion can be determined as a ratio between the concentration $[\text{DNA-BNNTs}]$ of the bound BNNTs and the total concentration $[\text{BNNTs}]_{tot}$ of the synthetic material and described by the Hill equation:

$$\frac{[\text{DNA-BNNTs}]}{[\text{BNNTs}]_{tot}} = \alpha \frac{[\text{DNA}]^n}{K_D + [\text{DNA}]^n} + B \tag{3}$$

where the parameter α is a proportionality factor, B accounts for background due to impurities, and K_D and n are empirical parameters. Fitting the curve in Figure 2B results in $\alpha = 0.56$ with $B = 0.11$, $K_D = 1.36 \times 10^{-9}$, and the Hill coefficient $n = 4.7$, reflecting positive cooperativity of the interactions ($R^2 = 0.97$).

The postsynthesis purification of an as-grown BNNT material is important for producing aligned solid materials such as films and fibers with outstanding properties.[15,35] Here, we demonstrate the purification of aqueous dispersions of DNA-BNNTs via a membrane filtration method and self-assembly of aligned BNNT films from a concentrated dispersion of purified DNA-BNNTs. After filtration, BNNTs can be easily resuspended in DI water by vortex mixing due to the DNA coating on the nanotube surface. Figure 3 compares absorbance spectra of a purified DNA-BNNT dispersion by

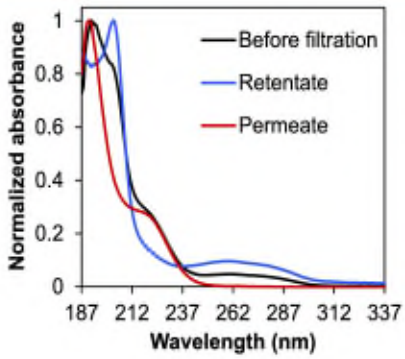

Figure 3. Absorbance spectra of $(GT)_{20}$-BNNT aqueous dispersions before and after membrane filtration of a stock dispersion of BNNTs:DNA = 1:1 (mass basis) using a centrifugal filter with a molecular weight cutoff of 30 kDa.

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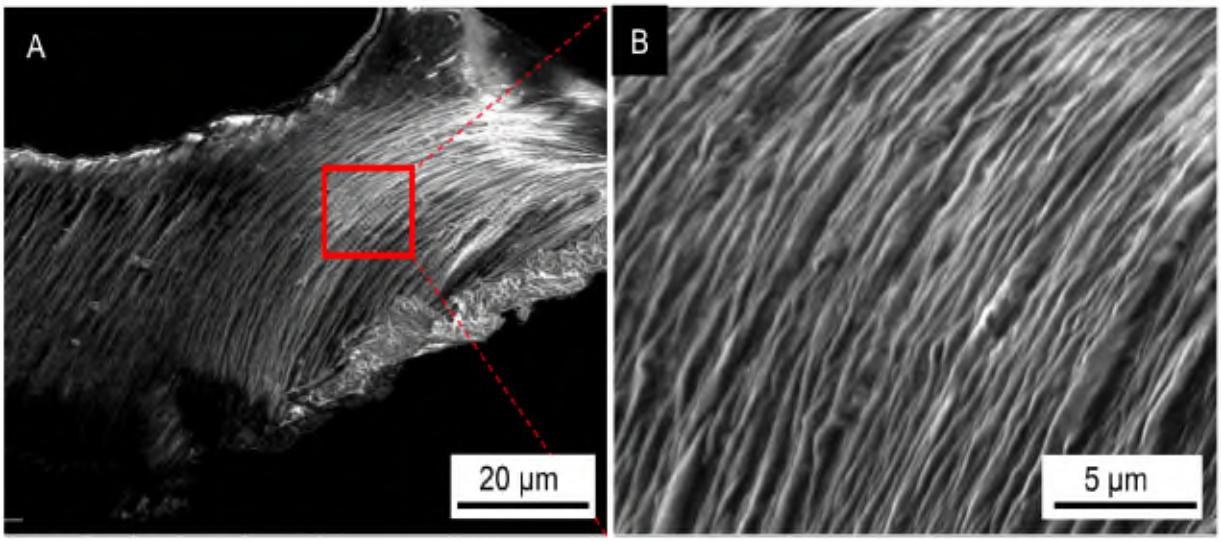

Figure 4. (A) SEM image of an aligned DNA-BNNT film formed by solvent evaporation of purified dispersions of BNNTs:DNA = 1:0.75 mass ratio (≈11.5 mass % of DNA-BNNT hybrids) without applied shear. (B) Surface morphology of the film showing the alignment of densely packed nanotube bundles.

membrane filtration with that of a stock dispersion. A dominant absorption peak at 205 nm corresponding to that of a DNA-BNNT hybrid was clearly observed for purified DNA-BNNTs collected in the retentate after membrane filtration. We speculate that the manifestation of a side band near 260 nm in the purified sample is intrinsic to BNNTs and may provide valuable information about phonon bands and optical activities relating to BNNT structures in future work.[36] In addition, the decrease in characteristic peaks at 190 and 220 nm corresponding to that of non-nanotube impurities such as elemental boron and *h*-BN structures for purified DNA-BNNT dispersions as well as the maintenance of those peaks in the permeate indicate the effective removal of the majority of impurities by filtration. Our purification approach produced DNA-BNNT dispersions that are highly enriched in individually dispersed nanotubes compared to those obtained from heat treated BNNT material, which was aimed primarily for eliminating elemental boron from an as-synthesized BNNT material (see the Supporting Information).[14]

The microstructure of purified DNA-BNNT dispersions at increasing concentrations of nanotubes was characterized by optical microscopy. Notably, uniform dispersions of nanotubes were maintained when evaporating a low concentration dispersion of purified $(GT)_{20}$-BNNTs containing an excess of DNA to as high as ≈11.5 mass % of DNA-BNNT hybrids (see the Supporting Information). Solid BNNT films were fabricated by allowing concentrated and purified dispersions (≈11.5 mass % of DNA-BNNT hybrids) to dry on a plasma treated silicon substrate without applied shear at ambient conditions. SEM of these films (Figure 4) revealed an aligned, densely packed structure composed of DNA/BNNT bundles after solvent removal. The bundles size was measured to be 143 ± 30 nm in diameter. To our knowledge, this is the first demonstration of solid BNNT films produced by spontaneous alignment of DNA-BNNT hybrids. The spontaneous alignment of BNNTs obtained in dried solid films may be driven primarily by an increase in BNNT translational entropy with the reduction in BNNT excluded volumes as the nanotube concentration increases with solvent evaporation. This phenomenon has been the subject of many current studies involving self-assembly of anisotropic building blocks where the ordering is driven by maximizing entropy.[37,38] In addition, emerging advances in the self-assembly of mesogenic nanomaterial dispersions,[39] including SWCNTs,[16,28,40] provide a foundation to better understand relationships between the phase behavior of DNA-BNNT dispersions, properties of solid assembled materials, and their processing conditions in future work. These important parameters will include the concentration and alignment of nanotubes in the dispersion precursor, substrate conditions, and shear and temperature during processing of solid films. Interestingly, the microstructure of aligned BNNT films resembles that obtained previously for solid films produced from a cholesteric liquid crystalline phase of SWCNTs stabilized by double-stranded DNA (dsDNA).[28] In addition, smooth surface morphology similar to that of dsDNA-SWCNT films was obtained due to uniform DNA coating of dried films while the alignment of nanotubes was observed beneath the outer thin layer of films. Our results indicate that DNA can effectively stabilize BNNTs in an aqueous environment and the removal of solvent by evaporating aqueous dispersions that are highly enriched in individually dispersed DNA-BNNT hybrids promotes the self-assembly of nanotubes into aligned films. This work could potentially provide a foundation to develop large area assemblies of BNNTs such as films and fibers with improved morphology and properties.

■ CONCLUSIONS

In summary, we have demonstrated a highly effective dispersion methodology of BNNTs in an aqueous environment using DNA and produced assembled solid films with improved nanotube alignment and purity. Similar to the binding of DNA to SWCNTs, our results showing the aqueous dispersion of DNA-BNNTs suggests the surface coating of nanotubes by DNA and the fraction of DNA-BNNT hybrids in dispersions depended on the BNNTs:DNA mass ratios. Purification of DNA-BNNT dispersions by membrane filtration resulted in the enrichment of dispersed nanotubes. Evaporation of

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concentrated, purified dispersions led to the formation of films comprising aligned DNA/BNNT bundles that has not been previously achieved. Our work establishes a method for the effective dispersion of BNNTs using biopolymer DNA, which may help guide the controlled and tailored liquid phase processing of BNNTs for applications in multifunctional materials, such as films and fibers with enhanced properties for thermal interface material, protective fabrics, and electronic and optoelectronic applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.9b00088.

Figures S1−S9 and experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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