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Functionalization, Dispersion, and Cutting of Boron Nitride Nanotubes in Water

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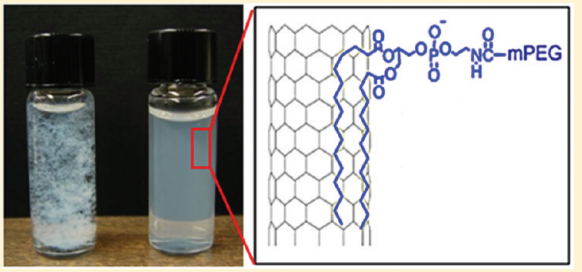
Supporting Information

ABSTRACT: High-quality boron nitride nanotubes (BNNTs) were functionalized for the first time with water-soluble and biocompatible PEGylated phospholipid [methoxy-poly(ethylene glycol)-1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-*N* conjugates (mPEG-DSPE)]. We found that BNNTs can be suspended in water for more than 3 months without precipitation. By comparing the dispersion stability of mPEG-DSPE/BNNTs in various solvents and the related Hansen solubility parameters, we found that polarized and hydrogen bonds between water and the hydrophilic mPEG play important roles in maintaining stable dispersion of BNNTs and preventing aggregation of mPEG-DSPE/BNNTs in the solutions. This has led to the formation of composite films with well-dispersed BNNTs and the coating of self-assembled monolayer (SAM) BNNTs. Furthermore, the lengths of these functionalized BNNTs can be shortened, for the first time, from >10 μm to ~500 nm by ultrasonication. Experiments suggest that effective dispersion of BNNT in solution is necessary for such cutting, where effective energy transfer from the sonicator to nanotubes is achieved. Our results will form the basis for stable functionalization, dispersion, and effective cutting of BNNTs with water-soluble and biocompatible PEGylated phospholipid, which are important for biomedical and composite applications.



1. INTRODUCTION

Carbon nanotubes (CNTs) are promising as the drug carriers to cells for various biomedical applications including cancer therapy. Toxicity of CNTs was a debatable issue as previous studies were performed using long and unfunctionalized CNTs, which tend to entangle in the biological systems and lead to various lung lesions and blocking of the airways.[1,2] More recent in vitro and in vivo studies indicate that high-purity single-walled CNTs are nontoxic when functionalized as hydrophilic nanomaterials.[3−7] Furthermore, in vitro investigation showed that water-soluble, short length (100−300 nm) CNTs exhibit longer blood circulation times and lower uptake by the reticuloendothelial system (RES).[8]

Boron nitride nanotubes (BNNTs) are structurally similar to CNTs and potentially useful for biomedical applications.[9,10] In particular, BNNTs offer unique potentials for boron neutron capture therapy (BNCT) because boron has a very high neutron capturing cross section. In addition, BNNTs are proven to have extraordinary mechanical properties comparable to that of CNTs.[11,12] Therefore, there are increasing interests in exploring the application of BNNTs in other areas for high-strength composites, radiation shielding in space vehicles, and nuclear reactor facilities. The key step toward all of these applications is to disperse functionalized BNNTs in organic solvents[13,14] and water. However, noncovalent functionalization of BNNTs in water is merely unexplored.[15−17] In particular, the stability of the dispersed BNNTs in water was not emphasized and investigated prior to biological experiments. In fact, toxicity of BNNTs on human embryonic kidney (HEK293) cells was recently found,[18] contradicted to a prior report.[15] Because short nanotube length was reported as an essential factor for CNTs to be biological compatible without causing accumulation and toxicity in the tested animals,[8,15] it is thus important to establish the mechanism behind functionalization of BNNTs in water, their dispersion stability, as well as exploring possible length shortening processes.

In this Article, we show that multiwalled BNNTs can be well-dissolved and dispersed in water through functionalization with methoxy-poly(ethylene glycol)-1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-*N* conjugates (mPEG-DSPE, Figure S1 of the Supporting Information). This PEGylated phospholipid is biocompatible and soluble in aqueous and organic solutions. The dispersion of these mPEG-DSPE functionalized BNNTs (mPEG-DSPE/BNNTs) is stable for more than 3 months without noticeable aggregation. The functions of mPEG, DSPE, and solvents are then systematically scrutinized. Furthermore, we found that long hour ultrasonication process can shorten the initial lengths of BNNTs (>10 μm) to below 500 nm. We believe that these findings are important to implement BNNTs in future biomedical applications.

2. EXPERIMENTAL SECTION

BNNTs were synthesized by our growth vapor trapping (GVT) approach in a conventional horizontal CVD furnace, as

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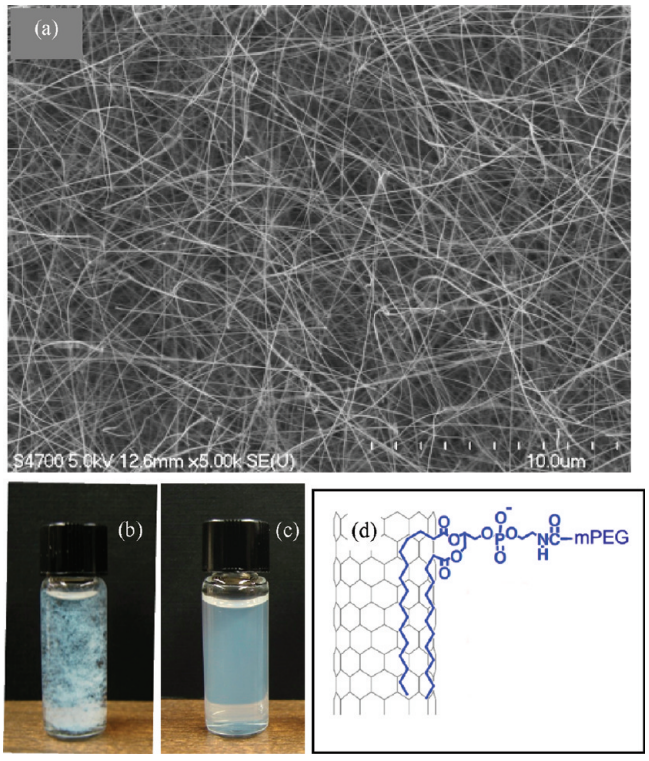

Figure 1. (a) Appearance of as-grown BNNTs on a Si substrate and (b) the extracted BNNT bundles in ethanol. (c) Well-dispered mPEG-DSPE/BNNTs in water (after 2 h of sonication). (d) Schematic representative of a BNNT functionalized by a mPEG-DSPE molecule.

previously reported.[19,20] These high-quality BNNTs have a band gap of ~6.0 eV, approaching the hexagonal phase BN single crystals. In this work, mPEG-DSPE (average molecular weight: 5000, purchased from Laysan Bio) was chosen as a polymeric system to functionalize BNNTs by forming stable protective coatings around the side walls of BNNTs. mPEG-DSPE, as one type of PEGylated phospholipid, has been widely used for targeted drug delivery research.[21] The overall molecular structure of mPEG-DSPE is illustrated in Figure S1 of the Supporting Information. As shown, mPEG is a derivative of PEG, in which one end of the molecule is terminated with a CH_3 group, instead of the OH.

In our experiments, ~1 mg of BNNTs was mixed into 200 μM mPEG-DSPE solution with 5 mL of DI water. The mixture was then sonication for 2 h. The mixture was further centrifuged at 3000 rpm for 1 h to remove unsuspendable impurities or entanglement of nanotubes. For a cutting experiment, a well-dispersed and stable BNNTs solution was sonicated in an ultrasonication bath (Branson, model 1210, 117 V, 1.3A) for various cumulative durations (up to 30 h). A small drop of the mixture was collected on a Si substrate and was then evaporated on a hot plate. The sample was annealed in air at 500 °C for 30 min to decompose the polymeric film, before imaging under SEM (Hitachi S-4700 FE-SEM) and TEM (JEOL JEM-4000FX). FTIR and Raman spectra were collected using a Jasco IRT-3000 FTIR microscope and Jobin-Yvon LabRAM HR800 Raman spectrometer, respectively.

3. RESULTS AND DISCUSSION

3.1. Functionalization of BNNTs with mPEG-DSPE. Our as-grown BNNTs have a typical length of more than 10 μm and

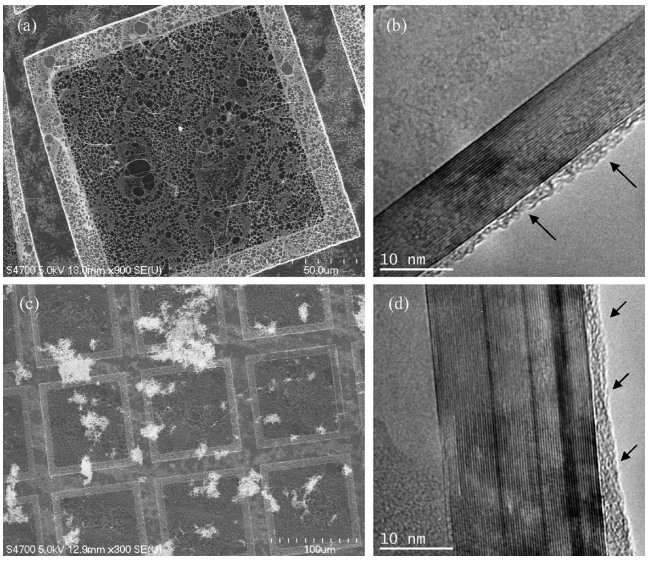

Figure 2. (a) Well-dispersed mPEG-DSPE/BNNTs in water when deposited on a TEM grid. (b) Amorphous coatings (mPEG-DSPE, as marked by arrows) on the side wall of a BNNT. (c) mPEG-DSPE/BNNTs suspended in ethanol forming clumps on the grid. (d) BNNTs in ethanol also coated with mPEG-DSPE (as marked by arrows).

nominal diameters of 50−80 nm (Figure 1a). These BNNTs can be extracted from Si substrates and form bundles in ethanol (Figure 1b). A stable milky solution was formed after the solution was mixed with mPEG-DSPE and sonicated for 2 h (Figure 1c). These well-dispersed mPEG-DSPE/BNNTs in water can form a stable solution for months without obvious clustering or precipitation. Figure 1d schematically illustrates a mPEG-DSPE molecule adsorbed on a BNNT, where two fatty acid chains from DSPE adsorb or wrap around BNNTs, whereas mPEG is hydrophilic and helps to disperse functionalized BNNTs in water solution. It is anticipated that the fatty acid chains have a strong tendency to adsorb on or wrap around the side wall of BNNTs via van der Waals forces, charge transfer, or hydrophobic interactions.[22−24] As a comparison, experiments were repeated for comparing cases with water and ethanol as the solvents. In contrast, mPEG-DSPE/BNNTs in ethanol could not form a stable solution (Figure S2 of the Supporting Information). Further examination on the supernatant of both types of mPEG-DSPE/BNNT solutions after 24 h was conducted with SEM. As presented in Figures S2c and S2d of the Supporting Information, suspended BNNTs in water can be transferred to substrates, but no BNNTs could be found in the ethanol solution as most BNNTs are precipitated and condensed. In fact, all BNNTs would condense in ethanol within 24 h, whereas those suspended in water with mPEG-DSPE remained stable for several months.

The suspension of the solutions was further investigated under TEM. The samples were prepared by putting one or two drops of the suspension on a lacey-carbon coated TEM grid. As shown in a low magnificent SEM image (Figure 2a), mPEG-DSPE/BNNTs suspended in water could be well-dispersed and coated on a TEM grid. Figure 2b is a typical high-magnified TEM image, revealing that an atomic amorphous layer was coated along the side wall of a nanotube. Because our as-grown BNNTs are free of amorphous coatings, we considered that these coating are mPEG-DSPE. mPEG-DSPE/BNNTs freshly suspended in ethanol were bundled on a TEM grid (white clumps in Figure 2c), which indicated a

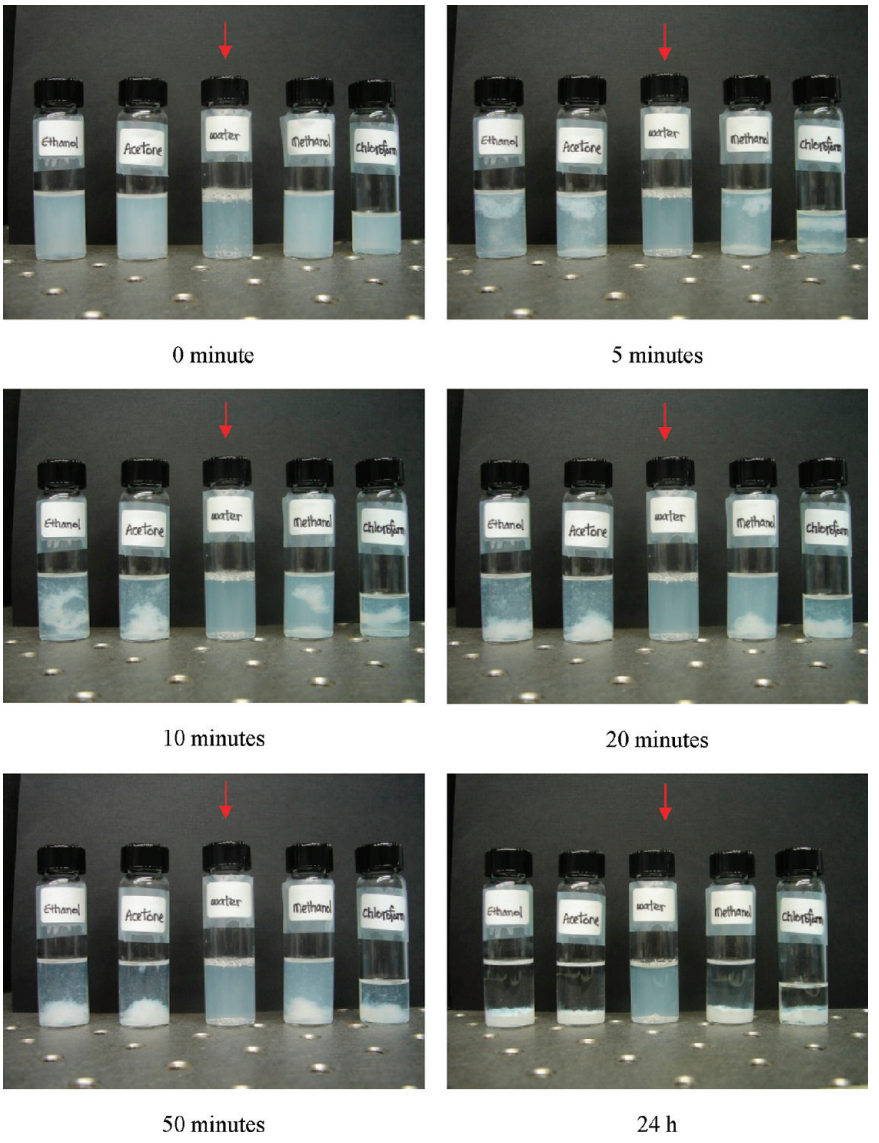

Figure 3. Series of photographs after various period of time showing the dynamic of sediments with different solvents (from left to right: ethanol, acetone, water, methanol, and chloroform). Only water can produce a stable milky BNNT solution (as marked by arrows).

poor dispersion. We found that most BNNTs could also be functionalized with mPEG-DSPE in ethanol, as depicted from a high magnification TEM image (Figure 2d). This result suggests that mPEG-DSPE dissolved in ethanol could also adsorb on BNNTs. However, the interaction between these mPEG-DSPE and ethanol is different than that in water, which leads to different degree dispersion stability and will be further discussed hereafter.

Poor dispersion of functionalized BNNTs in ethanol implies that suspension and dispersion of mPEG-DSPE/BNNTs is solvent dependence, although mPEG-DEPE is also dissolvable in most organic solvents. The interaction of solvent molecules with mPEG-DSPE/BNNTs could affect the efficiency of dispersion. It is thought that the molecular interaction between mPEG-DSPE and ethanol is weaker compared with that with water. Hence, gravitational force can slowly dominate to cause a condensation of nanotubes. To verify this hypothesis, we further investigated the solubility of mPEG-DSPE/BNNTs in different solvents. A series of photographs with different organic solvents was taken to show the dynamics of the precipitation. As presented in

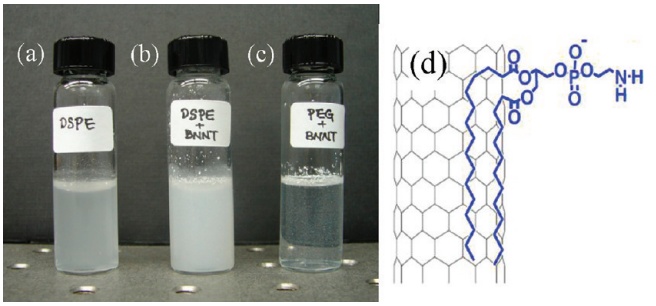

Figure 4. Appearances of (a) DSPE dispersed in water, forming a liposomes solution, (b) DSPE/BNNTs dispersed in water, and (c) PEG/BNNTs dispersed in water. (d) Schematic of a DSPE molecule interacting with a BNNT.

Figure 3, we show that mPEG-DSPE/BNNTs can only form a stable solution in water rather than acetone, methanol, chloroform, as well as ethanol. As suggested in Figure 1d, the hydrophilic

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interaction between the mPEG chains with the solvent is the key of suspension of mPEG-DSPE functionalized BNNTs. Comparing the properties of these solvents (see Table S1 of the Supporting Information[25]), it is evident that the Hansen solubility parameters (HSPs) for the polar (δ_P) and the hydrogen bonding (δ_H) interaction of water are significantly higher than those of other solvents. Consistent with these HSPs, we think that polarized bonds of water molecules play an important role in enhancing intermolecular forces between water and mPEG-DSPE/BNNTs and prevent precipitation of BNNTs by the gravitational force. Because of the nature of PEGylated phospholipids, the polar phosphates from DSPE as well as the hydrophilic mPEG chains interact with water molecules to form a stable BNNT solution. Furthermore, organic solvents tested here may also interact with the fatty acid chains of DSPE and reduce their interaction strength with BNNTs in organic solvents.

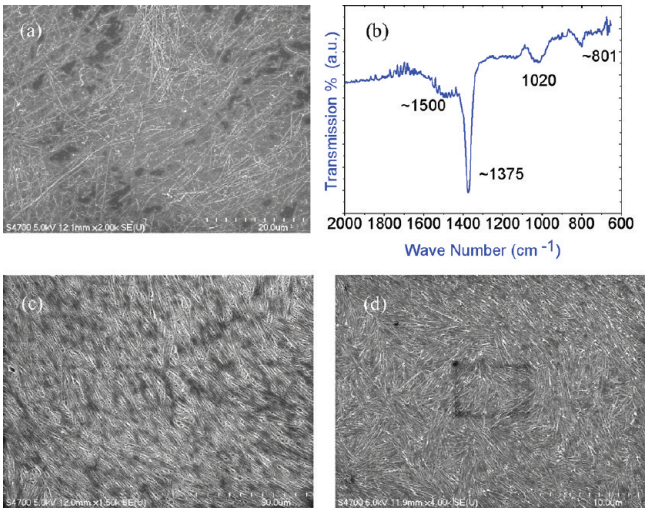

Figure 5. (a) SEM image of dispersion BNNTs revealed after the annealing process at 500 °C for 30 min in air and the (b) corresponding FTIR. Closely packed SAM BNNT films (c,d) detected at the edges of the dried solution droplet.

3.2. Comparing Functionalization of BNNTs with mPEG and DSPE. To understand further the solubility mechanism, we functionalize BNNTs with mPEG (Sigma-Aldrich, CAS no.: 9004-74-4, MW: 5000 g/mol) and DSPE (Sigma-Aldrich, CAS no.: 1069-79-0, MW: 748.07 g/mol), respectively. For these experiments, 10 mg of mPEG was mixed with ~1 mg BNNTs in 5 mL of DI water, whereas 5 mg DSPE was mixed with 1 mg BNNTs in 5 mL of DI water. In this case, more mPEG was used to increase its concentration due to its larger molecular weight. Both samples were then sonicated for 30 min in a sonication bath. As shown in Figure 4a, DSPE forms a milky liposomes solution in water, whereas the hydrophilic mPEG form clear solution in water (not shown). We found that BNNTs can be suspended in DSPE solution (Figure 4b). BNNTs could not be dissolved in mPEG solution (Figure 4c) and all BNNTs were aggregated and floated on the mPEG solution. Unlike most functionalization via $\pi-\pi$ interaction, it is anticipated that fatty acid chains/tails from

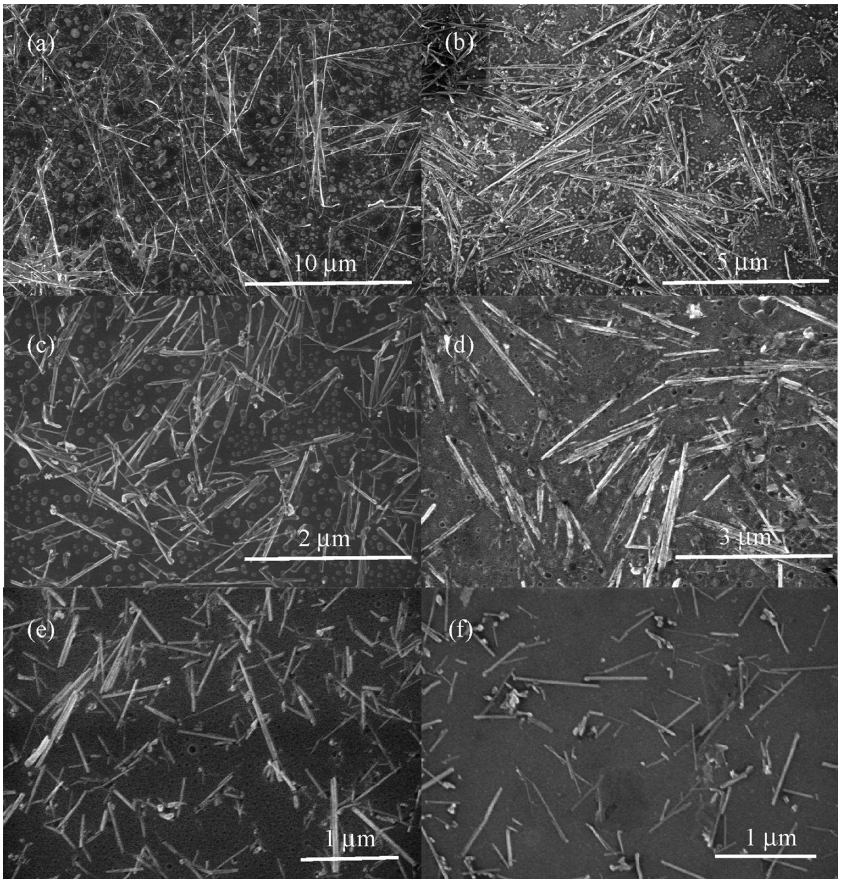

Figure 6. SEM images of shorterned BNNTs after various sonication durations of (a) 10 min, (b) 5 h, (c) 10 h, (d) 15 h, (e) 20 h, and (f) 30 h. As shown, the lengths of these BNNTs decrease with the increase in the cumulative sonication duration.

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DSPE have a strong tendency to adsorb on or wrap around the side wall of BNNTs via van der Waals forces, charge transfer, or hydrophobic interactions.[22−24] The hydrophilic phosphate group of DSPE is responsible to interact with the water molecules and help to suspend BNNTs in water, as illustrated in Figure 4d. However, the linkage of mPEG on DSPE will further enhance the solubility of BNNTs in water due to the longer hydrophilic molecular chains and thus create extended distances between BNNTs to avoid bundling and subsequent precipitation.

3.3. Formation of Monolayer BNNT Films. We further examine the use of these functionalized BNNTs in the preparation of composite films on substrates. This was performed by coating a drop of mPEG-DSPE/BNNT solution onto a clean Si substrate. The substrate was heated up on a hot plate. When water was evaporated from a substrate, BNNTs was embedded in a form of polymeric composite. The present of BNNTs could hardly be imaged under SEM, due to the charging effect from the insulating polymers and BNNTs (inset of Figure S3 of the Supporting Information). As confirmed from the FTIR spectrum (Figure S3a of the Supporting Information), polymeric spectrum was dominated, which is almost identical to that of mPEG-DSPE, as presented in Figure S3b of the Supporting Information.

To examine the degree of BNNT dispersion in these composite films, the excessive polymeric film was decomposed by annealing at 500 °C for 30 min in air. A monolayer of BNNTs was found everywhere on a substrate, indicating good dispersion of the nanotubes (Figure 5a). FTIR spectrum with characteristic peaks of BNNT at ∼1375, ∼1500, and ∼801 cm^{-1} was revealed after annealing (Figure 5b). There was an additional absorption band at ∼1020 cm^{-1} in the spectrum, which corresponds to additional SiO_2 layered formed on the substrate during the annealing process.[26] It is also interesting to note that functionalized BNNTs can be easily dispersed on a substrate by drop casting, forming self-assembled monolayer (SAM) BNNT films. Denser BNNTs are found near the edge of the suspension droplet due to the capillary force of the drying liquid. Occasionally, BNNTs can be closely packed and self-aligned over an area of millimeter square. In addition, we observed that lower density and longer BNNTs (>10 μm) are harder to self-align, perhaps even not possible due to larger aspect ratio.

3.4. Cutting of BNNTs. Figure 6 presents a series of SEM images of BNNTs after various durations of sonication. These images are shown at different magnification factors to capture the actual length of BNNTs after sonication. As shown, the length of BNNTs was ∼10 μm after a brief sonication of 10 min. The lengths of BNNTs continued to reduce when sonication was applied for longer duration (Figure 6a−f). A quantitative analysis was also performed to confirm the observation by obtaining an average length. For each sample, at least 40 nanotubes were randomly selected from two SEM images to measure their length manually. Standard deviation was used as an estimation of statistical errors. These results are summarized in Figure 7a. In general, the average length of BNNTs could achieve ∼1 μm after 10−20 h sonication. BNNTs with length <500 nm were obtained after 20−30 h of sonication. As also shown in the Figure 7a, the estimated nanotube length after 15 h of sonication is longer than that obtained after 10 h. We believed that this is due to the statistical deviation during the length estimation process because there would be some longer BNNTs in the starting materials that needed longer sonication for length shortening. These are the BNNTs that appeared longer than others after sonication and were randomly sampled in this length estimation. TEM images of

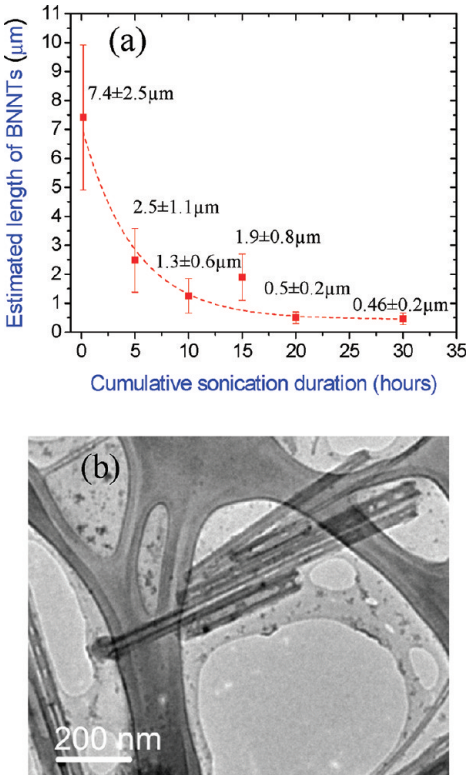

Figure 7. (a) Measurement and statistically analysis of the nanotube length after various cumulative sonication duration and (b) TEM image of the shortened BNNTs.

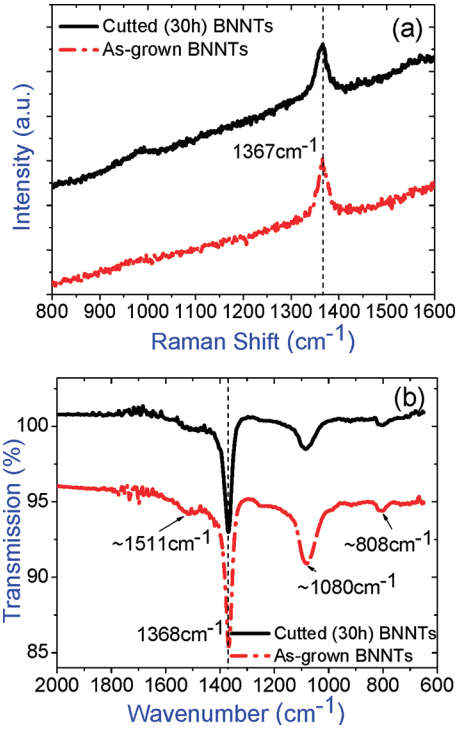

Figure 8. (a) Raman and (b) FTIR spectra of as-grown and cutted BNNTs.

BNNTs after the 30 h of sonication are shown in Figure 7b. As shown, the nanotube structure is resilient and partially filled with

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the mPEG-DSPE solution. In addition, Raman and FTIR spectra of as-grown and cutted BNNTs are compared in Figure 8a,b, respectively. As shown, there is no significant difference between the spectra, indicating that the cutted samples preserve their intrinsic crystalline properties.

It is noted that uniform dispersion is important for these effective cutting. We observed that BNNTs cannot be cut without prior functionalization with mPEG-DSPE in water. We performed the same cutting experiment with functionalized BNNTs in ethanol suspension. No significant cutting could be obtained even up to 60 h sonication. Apparently, only well-soluble BNNTs in water produce systematically reduced length.

We think these cutting phenomena can be explained based on the mechanism of ultrasonic cavitation.[27−29] First of all, sonication treatment helps dispersing and debundling functionalized BNNTs in water. As sonication proceeds, near-surface damages will be created as BNNTs are exposured to the acoustic cavitation, shock waves, collisions, and shear forces. In general, bubbles or so-called cavities are created by the alternating expansion and compression of the acoustic waves. These bubbles oscillate, accumulate ultrasonic energy and grow in size. They can subsequently collapse in a short period of time and release the concentrated energy. As reported, this implosion produces intense localized and transient heating (∼5000 K), high pressures (∼1000 atm), enormous heating and cooling rates (>10^9 K/sec).[27,28] We suggest that these are the conditions that lead to the initiation of surface damages on BNNTs, which will then propagate into cutting. Assuming that the sonication energy per volume is uniform throughout the solution, well-dispersed nanotubes are spread through the entire volume and exposed to most sonication energy deposited from the cavitation. With poor dispersion in solution, BNNTs are confined at much smaller liquid volume, and thus the sonication energy deposited per nanotubes is much lower. The cutting efficiency therefore reduces. It should be noted that conventional cleaning sonication baths employed here may not be optimum for the cutting process. We believed that the duration for cutting can be further reduced with the use of high-power sonication instruments.

4. CONCLUSIONS

As a summary, we show that BNNTs can be easily functionalized and well-dispersed in water using a biocompatible PEGylated phospholipid molecule, mPEG-DSPE. From our results, the dispersion of these functionalized BNNTs depends on the type of solvent involved. Specifically, ethanol, methanol, acetone, and chloroform can dissolve mPEG-DSPE but cannot form stable mPE-DSPE/BNNT suspension. The solvent dependence suggests that the interaction between the hydrophilic PEG with these organic solvents is weaker compared with that with water. Besides, organic solvents may interact with fatty acid tails of phospholipids and reduce its functionality to bond with BNNTs. We also anticipate that the interaction of phospholipids and BNNTs is not due to $\pi-\pi$ interaction because there is no π orbital along the fatty acid chain of phospholids.

When the density of nanotubes is sufficiently high, these functionalized BNNTs can be self-aligned over areas of millimeter square simply by the surface tension and capillary force of the solution droplet when evaporated on the substrates. This behavior is most likely able to control the alignment of BNNTs by Langmuir−Blodgett trough after functionalization, as previously reported for CNT alignment.[30−32]

Furthermore, cutting of well-dispersed BNNTs (in this case, with mPEG-DSPE in water) was demonstrated for the first time. BNNTs can be cut from its original length of >10 μm to below 500 nm using long hour sonication process (>20 h). We show that both functionalization and stable dispersion are necessary for effective cutting of BNNT. It is proposed that shear force and collision generated by sonication act more effectively and continuously to well-dispersed nanotubes and help to break mechanically the B−N bonds near the defects located on the side walls of the nanotubes. We think that the phenomenon can be extended to any kind of PEGylated phospholipids. This process opens a way to functionalize BNNTs with biocompatible polymers and extend BNNT applications in biomedical and high-strength composites. Our approach could be useful for delivering BNNTs to targeted cells for cancer treatment, such as BNCT. Prior to these biomedical applications, further experiments are needed to test the stability of PEGylated BNNTs in various physiological solutions such as saline and serum.

■ ASSOCIATED CONTENT

Supporting Information. Hansen solubility parameters (HSPs) for the solvents, molecular structure of mPEG-DSPE, photographs of dispersion of mPEG-DSPE/BNNTs in water and ethanol, and FTIR spectra of polymeric films (a) with and (b) without BNNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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