Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

A Thermodynamic Approach to Boron Nitride Nanotube Solubility and Dispersion

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Characterization of As-Synthesized BNNTs

The raw BNNT material used in this work was thoroughly characterized prior to use. Figure 1 shows representative transmission electron microscope (TEM) micrographs for raw BNNTs, with insets depicting a single-wall BNNT (SWBNNT), a double-walled BNNT (DWBNNT), and a multi-walled BNNT with 10 walls (10WBNNT). Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) micrographs of the raw BNNTs are shown in Figures S1A and S1B. The as grown BNNTs appear very thin and long with high aspect ratio, and shows flexible bundles of tubes with entangled tube aggregates. These representative images also show the presence of some boron nanoparticle impurities that are generated during the synthesis process. Note that the nanotubes were not purified prior to the dispersion studies, but it was not expected that the presence of boron nanoparticles would alter the outcome of this study. In addition to their different composition and morphology of these nanoparticles, they possess a much smaller surface area compared with BNNTs, are denser than BNNT (~2.3 vs 1.4 g/cm^3), and are expected to have differing surface chemistry.

The thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and ultraviolet-visible spectroscopy (UV-Vis) characterization (Figure S2) was conducted to confirm the composition and quality of the as-synthesized material. The TGA thermogram demonstrates the excellent thermal stability of BNNTs (Figure S2A) up to ~800°C in air.The corresponding FTIR spectrum (Figure S2B) displays the expected peaks for the in-plane BN transverse optical mode and out-of-plane B-N-B bending mode at 1363 and 800 cm^{-1}, respectively.[S1] A third minor peak is observed at 3219 cm^{-1} which can be attributed to impurities (B-O, O-H, or N-H stretching), which suggests that there may be some minor contamination with oxygen and hydrogen during or after the BNNT synthesis.[S2] The FTIR spectra after 30min sonication is also shown in Figure S8. No noticeable peaks are found other than B-N modes. The UV-Vis spectrum (Figure S2C) shows a broad absorbance reaching a maximum at 207 nm, which corresponds to the band gap transition of BNNTs.[S3,S4] The TGA, FTIR, and UV-Vis results combined with the electron microscopy confirm that the raw material utilized in this work contains high-quality BNNTs.

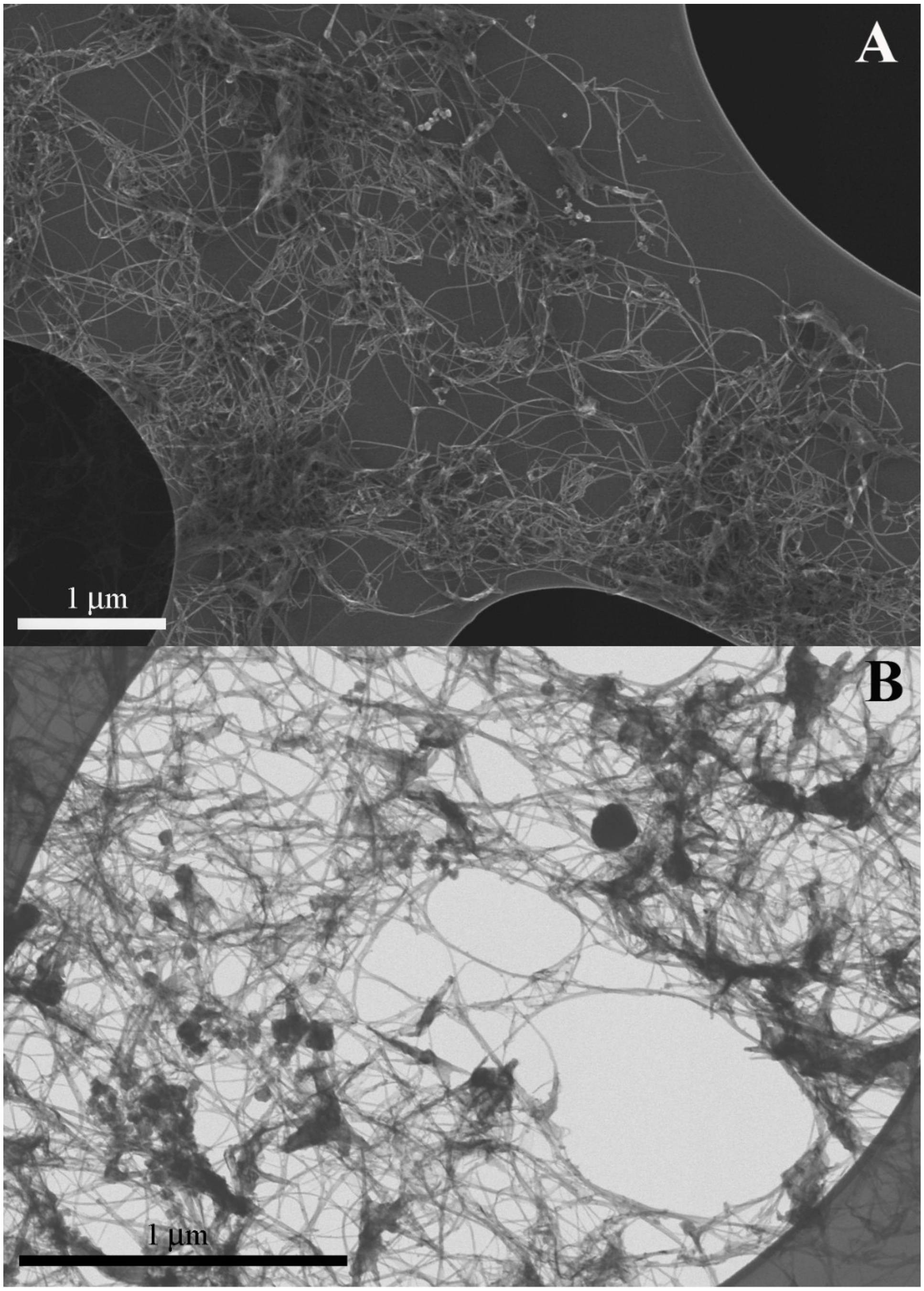

Figure S1. Representative SEM (A) and STEM (B) images of raw BNNT material utilized in this work.

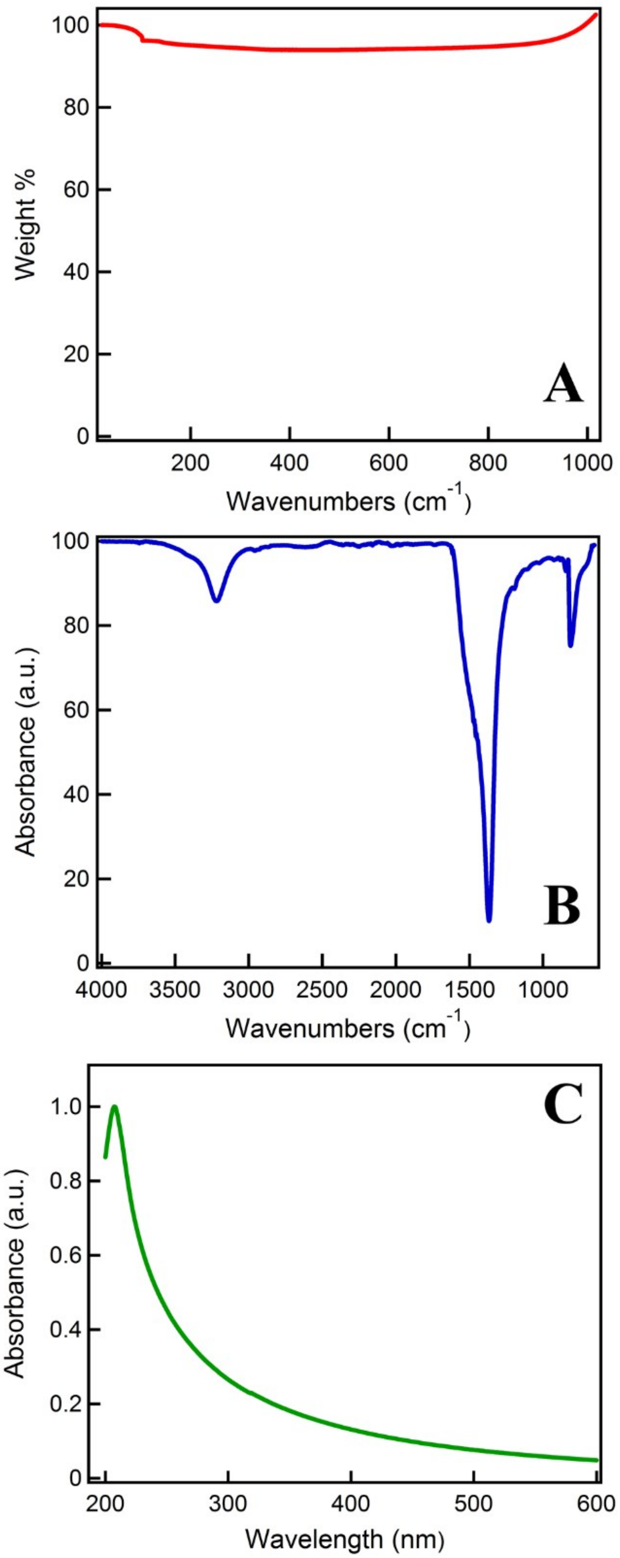

Figure S2. Characterization of as-synthesized BNNTs: TGA in air up to 1000°C (A), mid-IR spectrum from 4000 – 400 cm^{-1} (B), and UV-Vis spectra from 190 – 800 nm (C).

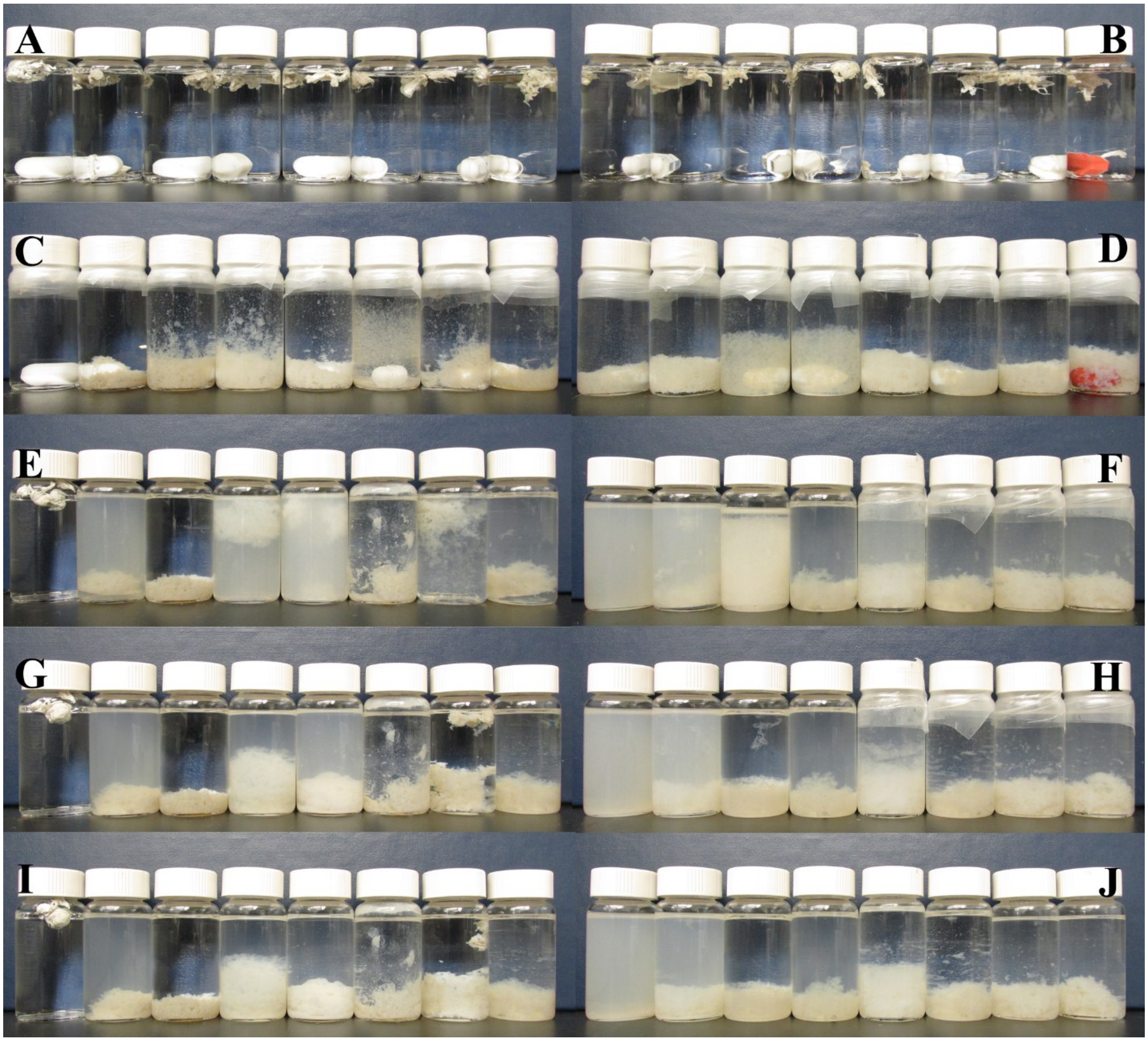

Figure S3. Images of all single solvent studies before stirring (A, B), immediately after stirring for 96 hours (C, D), immediately after sonication for 30 minutes (E, F), after settling for 24 hours (G, H), and after settling for 1 week (I, J). The samples in A, C, E, G, and I from left to right are water, acetone, ethanol, isopropanol, methanol, hexane, acetic acid, and toluene. The samples in B, D, F, H, and J from left to right are DMAc, DMF, DMSO, NMP, THF, pyridine, chloroform, and dichloromethane. Note that all stir bars were removed from the sample vials prior to sonication (E-J).

Additional Discussion on Solubility Effects:

Another factor that should be considered in terms of BNNT dispersion is molecular size of both the solvent and the solute. Smaller solute molecules are more readily soluble while smaller solvent molecules can diffuse faster. As a result, Hansen has proposed that the molecular volume should be treated as a fourth Hansen solubility parameter.[40] However, molecular size effects are a kinetic effect, not a thermodynamic one, and its incorporation into a new set of blended solubility parameters has not been successful. Still, these effects should not be ignored. In some instances, smaller molecular species (*i.e.* acetone and methanol) may be able to effectively disperse a given solute although their solubility parameters are outside its solubility region. This may be the case in this work, as MeOH was able to disperse BNNTs effectively but appeared more like an outlier based on the Hansen solubility parameters alone. The molar volumes (V_M) for the solvents utilized in this work were listed in Table S1.

Next, the surface tension (γ) values of the solvents tested were compared to investigate the efficacy of this value to identify good solvents. Yum and Yu experimentally determined the surface tension for individual BNNTs using the Wilhelmy method to be 26.7 mN/m.[49] Similar to the Hildebrand parameter, the BNNTs used in Yum and Yu's work were produced *via* CVD growth so the value may differ slightly for the HTP synthesized BNNTs used in this work. Table S1 shows the surface tension values for all of the single solvents. Comparing to visual observations, solvents with surface tension values in the range of 23.0 – 34.4 mN/m should be good solvents for BNNT. Indeed, this range encompasses the experimental value from Yum and Yu, but chloroform, dichloromethane, acetic acid, and toluene all lie within this region but were found to be poor solvents for BNNTs. Moreover, the surface tension of chloroform and tetrahydrofuran (26.7 mN/m) match the experimental value of BNNTs but displays very different dispersion states for BNNTs. Thus, these observations agree with those of Bergin *et al.*,[42] reinforcing that surface tension alone is not a viable parameter for identifying good solvents.

Table S1. Surface tension (γ_L), density, viscosity, and molar volume (V_M) for the solvents utilized in this work. The values listed are at 25°C unless otherwise noted.

Solvent	γ_L (mJ/m^2)	Density (g/cm^3)	Viscosity (cP)	V_M (cm^3)
N,N'-dimethylacetamide (DMAc)	32.43[a]	0.937	0.95	92.5
N,N'-dimethylformamide (DMF)	34.4	0.945	0.80	77.0
acetone	23.0	0.785	0.31	74.0
methanol	22.1	0.791	0.54	40.7
tetrahydrofuran (THF)	26.7	0.883	0.46	81.7
isopropyl alcohol (IPA)	23.4	0.785	1.96	76.8
N-methyl-2-pyrrolidone (NMP)	44.6	1.033	1.67	96.5
chloroform	26.7	1.479	0.12	80.7
dichloromethane	27.8	1.326	0.41	63.9
acetic acid	27.0	1.045	1.06	57.1
dimethylsulfoxide (DMSO)	42.9	1.092	1.99	71.3
toluene	27.9	0.867	0.56	106.8
pyridine	36.7	0.982	0.88	80.9
ethanol	22.0	0.789	1.07	58.5
hexane	17.9	0.659	0.30	131.6
water	72.7	1.000	0.89	18.0

[a]Given value for DMAc is at 30°C.

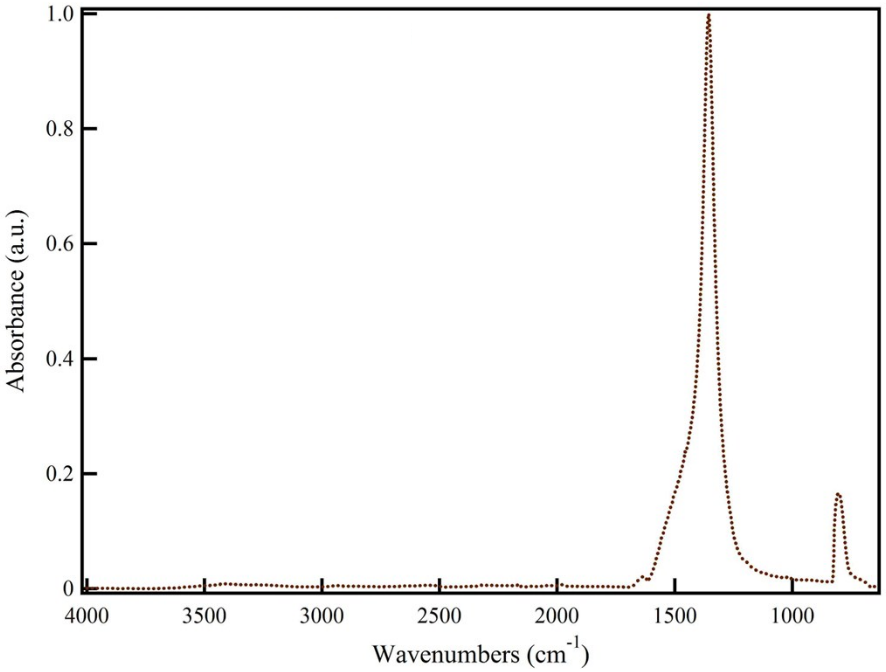

Figure S4. IR spectra of BNNT after 30min sonication. No noticeable peaks are shown other than B-N vibrations.

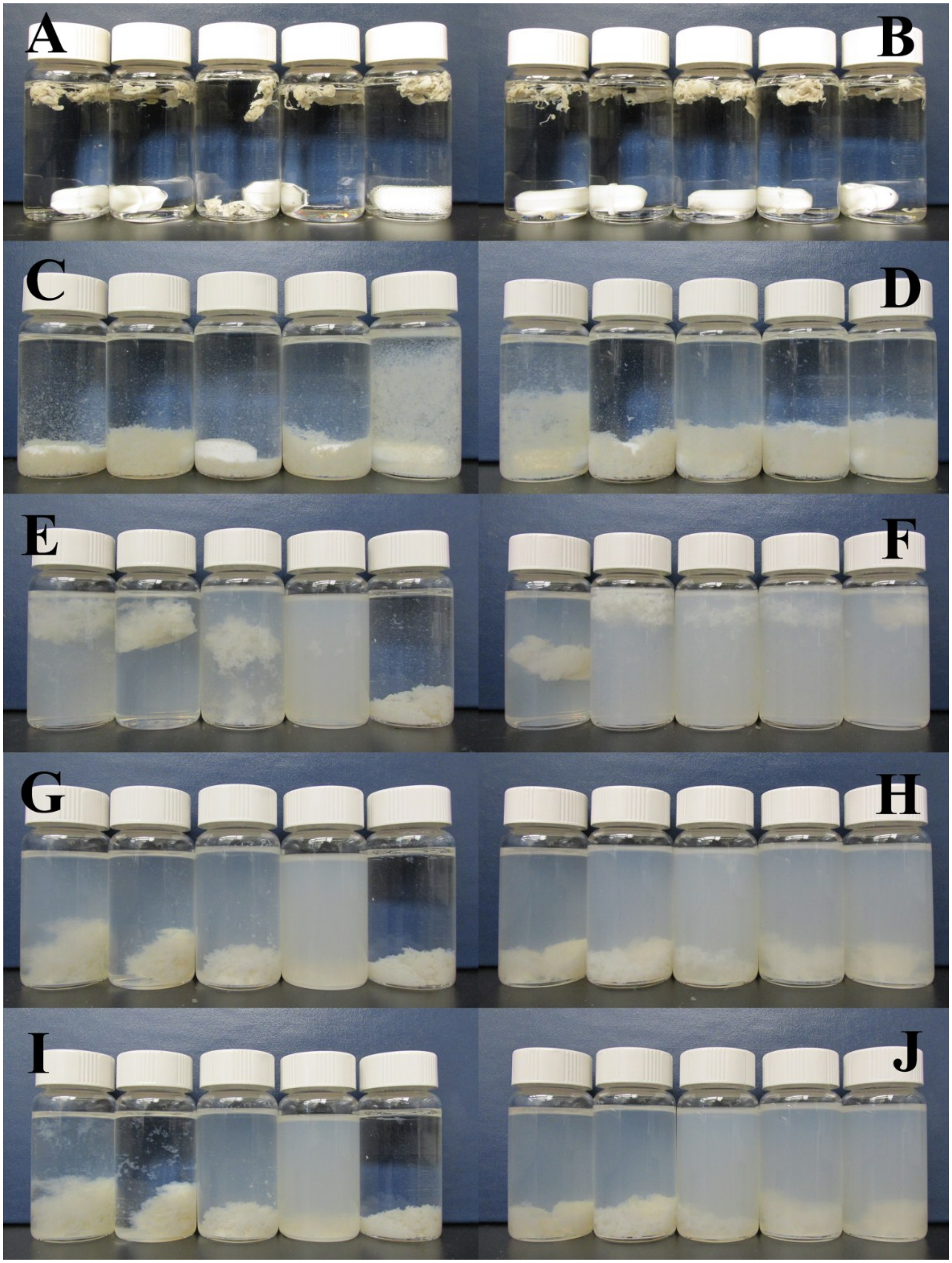

Figure S5. Images of all 1:1 co-solvent studies before stirring (A, B), after stirring for 96 hours (C, D), after sonication for 30 minutes (E, F), after settling for 24 hours (G, H), and after settling for 1 week (I, J). The samples in A, C, E, G, and I from left to right are IPA-DMF, DMF-DCM, THF-hexane, DMF-toluene, and DMAc-water. The samples in B, D, F, H, and J from left to right are DMAc-NMP, EtOH-acetone, DMF-acetone, THF-NMP, and DMSO-THF. Note that all stir bars were removed from the sample vials prior to sonication (E-J).

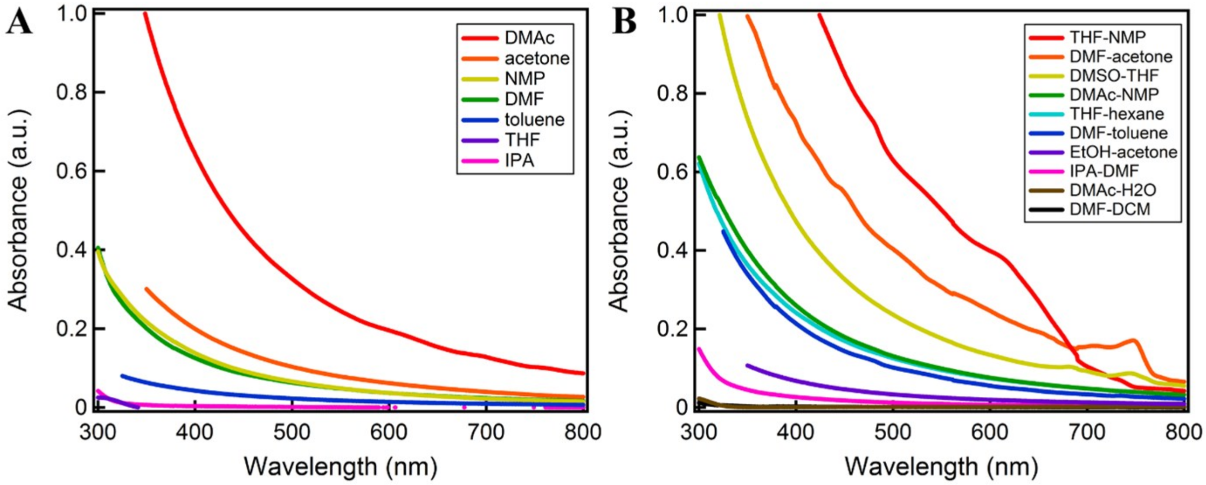

Figure S6. UV-Visible spectra for all BNNT single solvent (A) and co-solvent (B) dispersions after 2 months of settling time to demonstrate long-term stability relative to each other.

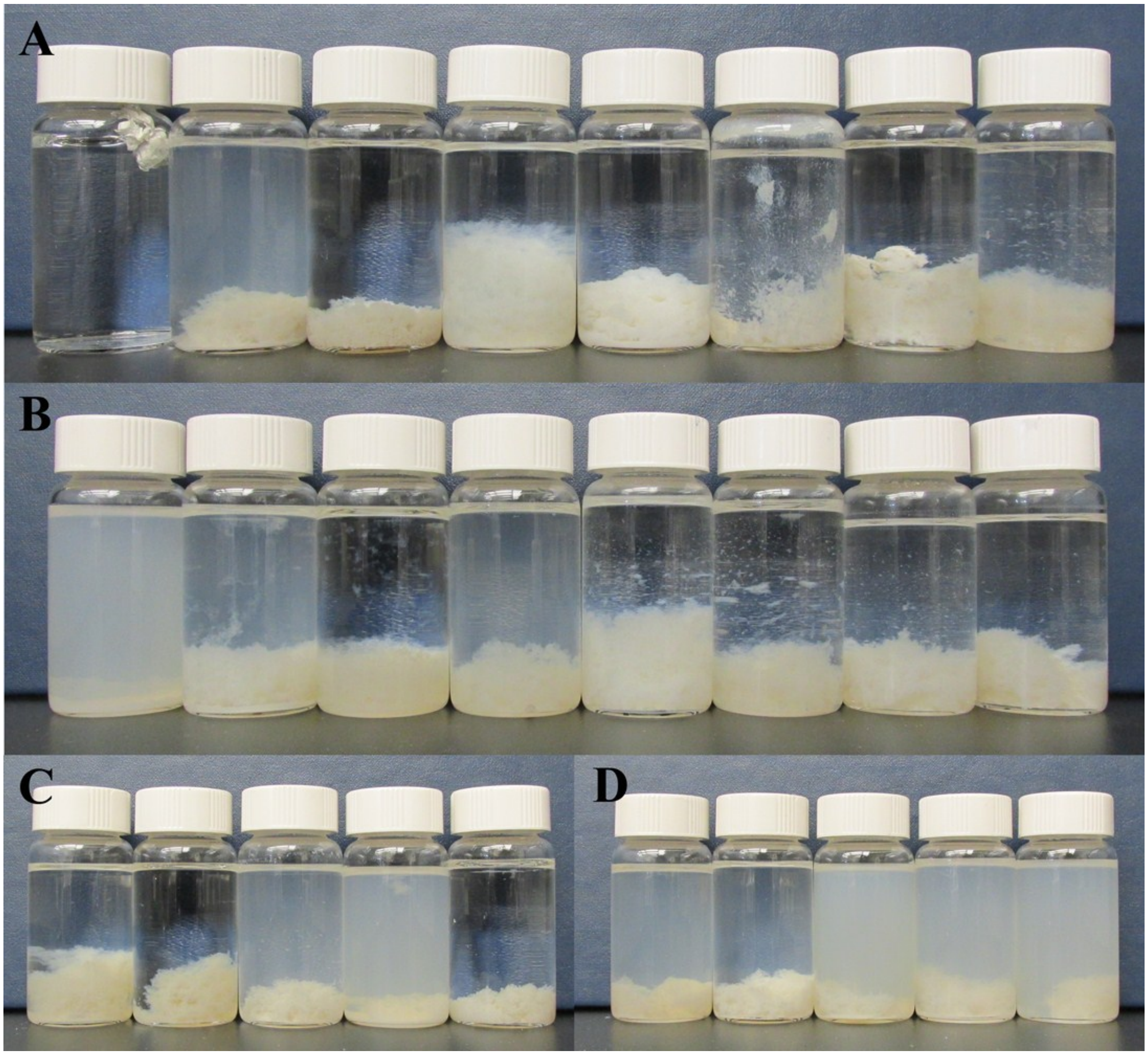

Figure S7. Images of all studies 1 month post sonication after settling for 1 week for single solvents (A, B) and co-solvents (C, D). The samples in A from left to right are water, acetone, ethanol, isopropanol, methanol, hexane, acetic acid, and toluene. The samples in B from left to right are DMAc, DMF, DMSO, NMP, THF, pyridine, chloroform, and dichloromethane. The samples in C from left to right are IPA-DMF, DMF-DCM, THF-hexane, DMF-toluene, and DMAc-water. The samples in D from left to right are DMAc-NMP, EtOH-acetone, DMF-acetone, THF-NMP, and DMSO-THF.

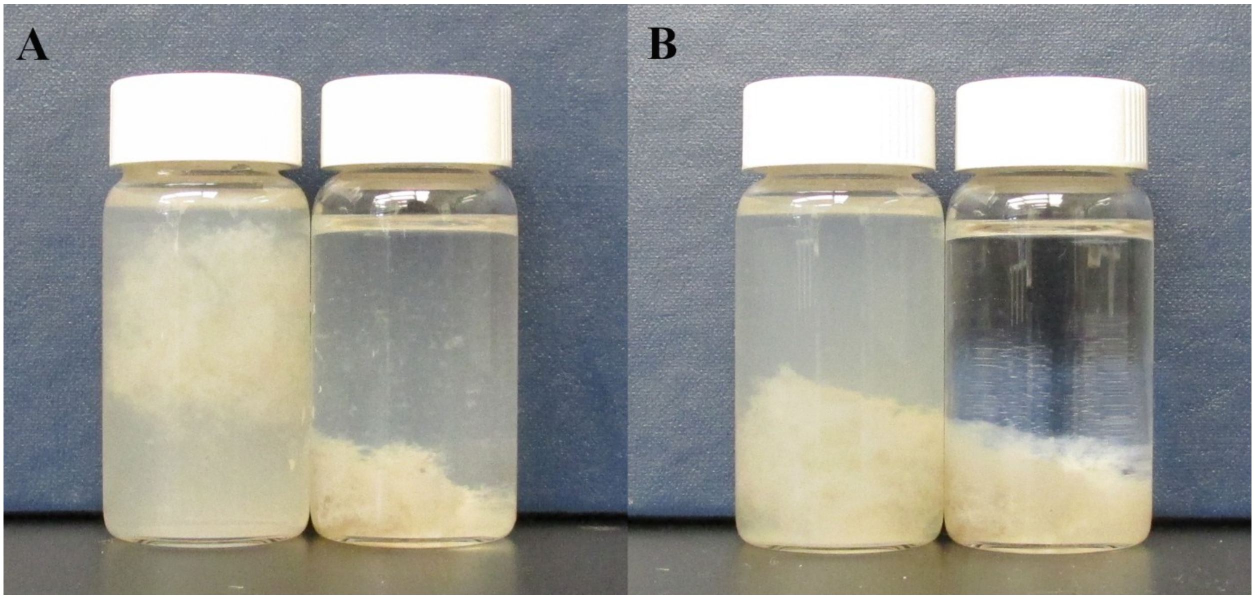

Figure S8. Images of BNNTs dispersed in a 85:15 mixture of THF-hexane (left vial) and 90:10 mixture of DMAc-water (right vial) immediately following sonication (A) and after 1 week of settling time (B).

References

S1. C. Zhi, Y. Bando, C. Tang, D. Golberg, R. Xie and T. Sekigushi, *Appl. Phys. Lett.*, 2005, **86**, 213110.

S2. K. S. Kim, C. T. Kingston, A. Hrdina, M. B. Jakubinek, J. Guan, M. Plunkett and B. Simard, *ACS Nano*, 2014, **8**, 6211.

S3. Z. Gao, C. Zhi, Y. Bando, D. Golberg and T. Serizawa, *J. Am. Chem. Soc.*, 2010, **132**, 4976.

S4. Z. Gao, C. Zhi, Y. Bando, D. Golberg and T. Serizawa, *ACS Appl. Mater. Interfaces*, 2011, **3**, 627-632.