New approach in the achievement of stable aqueous dispersions of carbon nanotubes

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Supplementary Information

Experimental Section

Multi-walled carbon nanotubes were acquired from Nanocyl (NC7000, purity of 90 %, 9.5 nm of diameter and 1.5 µm of length) and it was named as MWCNT; (6,5) enriched single-walled carbon nanotubes from Sigma-Aldrich (40 % of (6,5) chirality, purity of 95 %, diameter between 0.7 and 0.9 nm and mean length of 1.0 µm) and was named as SWCNT-A; HiPCO single-walled carbon nanotubes from Unidym (purity of 65 %, diameter between 0.8 and 1.2 nm and length between 100 nm e 1 µm) and was named as SWCNT-H. Tetrahydrofuran (THF) (99 %) was acquired from Neon, ethanol (99.5 %) from Nuclear, ethyl ether (99,7 %) from Merck, sodium chloride (99 %) from Vetec, acetone (99.5 %) from Neon, acetonitrile (>99.9 %), 2,6-di-tert-butyl-4-methylphenol (BHT) (99 %), benzene-1,4-diol (hydroquinone) (99 %), toluene (>99.9 %) from Sigma-Aldrich, n-hexane (99 %) from Synth, and phenol (98 %) from Grupo Química. Deionized water (18.2 MΩ) was obtained in an Elga Purelab Flex equipment. Bath ultrasonicator used to disperse carbon nanotubes is a UNIQUE-USC equipment, model 1880, with frequency and potency of 37 kHz and 154 W respectively, and interfacial thin films were prepared in a magnetic stirrer from IKA, model Color Squid, with maximum speed of 2500 rpm.

Both single-walled and multi-walled aqueous dispersions were prepared following the same procedure. THF was distilled with a microdistillation apparatus, at ambient pressure and collection one drop each 3 s. Carbon nanotubes were added to a 100 mL round-bottom glass flask, 0.5 mg of MWCNT or SWCNT-H and 0.2 mg of SWCNT-A together with BHT solution prepared in distilled THF, 10 mL of $5^{\times}10^{-4}$ mol L^{-1} BHT solution for MWCNT or 20 mL of $1^{\times}10^{-3}$ mol L^{-1} BHT solution for both SWCNT. The mixture was treated in bath ultrasonicator cooled with small portions of ice, and the mixture inside the round-bottom flask was totally immersed in the bath. MWCNT was sonicated for 1 h and both SWCNT were sonicated for 3 h. After sonication, 100 mL of deionized water was rapidly added to the organic dispersion and the resultant mixture was filtered with paper filter to another 100 mL round-bottom flask soon after water addition. The 100 mL flask was covered with rubber septum and two metal needles were connected to the septum. Purge was made with atmospheric air with approximate flux of 1 L min^{-1} for 48 h to eliminate most of THF maintaining the flux above the liquid surface. The dispersions were named according the solid material dispersed, for example SWCNT-A-H_2O is referent to aqueous dispersions prepared with SWCNT-A. It was prepared a blank dispersion without carbon nanotubes following the same procedure adopted to disperse MWCNT. This blank sample was named BHT-H_2O-B.

The amount of CNTs remaining in each stable dispersion was determined by taking a known volume of each dispersion, evaporating the water, treating the remaining solid at 350 °C for 2 h in ambient atmosphere and determining the mass of the resulting residue.

Critical coagulation concentration (CCC) of MWCNT-H_2O sample was determined with aqueous solutions of sodium chloride. Briefly, 4.5 mL of MWCNT-H_2O was added to 10 mL glass flask together with 4.5 mL of deionized water or sodium chloride solutions with concentrations equal to $2^{x}10^{-5}$, $2^{x}10^{-4}$, $2^{x}10^{-3}$, $2^{x}10^{-2}$ and $2^{x}10^{-1}$ mol L^{-1}, resulting in mixtures with sodium chloride concentration equal to half of the initial value. The mixtures were kept in rest for 12 h and then pictures were acquired.

Raman spectra of dispersions were collected in situ according the procedure described in the literature.[1–3] Raman spectrum of MWCNT-H_2O sample was acquired from 1000 to 2000 cm^{-1} using Ar^+ laser (λ = 514.5 nm). Raman spectra of SWCNT-A-H_2O and SWCNT-H-H_2O samples were acquired from 130 to 2000 cm^{-1} using Ar^+ laser and He-Ne laser (λ = 632.8 nm). All spectra of dispersions and pure water were acquired with 200 accumulations of 30 s each, using objective lens of 20x and adjusting the focus below the liquid-air interface. Raman spectra were normalized in respect to G band, then the solvent spectrum obtained with the same experimental conditions was normalized and subtracted from the dispersion spectrum, resulting in a subtracted spectrum that presents the characteristics bands of carbon nanotubes. The baseline of subtracted spectra was corrected, and bands were fitted with Lorentzian curves. Raman spectrum of MWCNT-H_2O sample has low intensity, so it was prepared a concentrated dispersion following the procedure described before and using 20 mL of $5^{x}10^{-4}$ mol L^{-1} BHT solution in THF to disperse solid MWCNT instead of 10 mL used previously and this concentrate dispersion was used only for Raman analysis.

Samples for GC-MS were prepared by liquid extraction. Briefly, 5.0 mg of MWCNT was added in a 100 mL round-bottom glass flask together with 50 mL of BHT solution ($1^{x}10^{-2}$ mol L^{-1}) in distilled THF. This mixture was sonicated in bath ultrasonicator for 1 h cooled with small portions of ice. After sonication, it was transferred to a 50 mL Beaker, 10 mL of deionized water was added and then the solvents were removed by heating the mixture at 353 K with heating plate and then in an oven at 343 K by 30 min. After cooling at room temperature, 20 mL of distilled ethyl ether was added to the Beaker. This mixture handled stirred and filtered with paper filter. Ether extracts was analyzed by GC-MS. The same process and analysis were performed for a similar sample without carbon nanotubes. The extract obtained from sample prepared with carbon nanotubes has an intense yellow color and the extract prepared without nanotubes has a slight yellow coloration and is almost transparent.

Thin films of carbon nanotubes were prepared following the procedure reported by our research group.[4–6] 20 mL of aqueous dispersions was added to a 50 mL round-bottom glass flask and stirred at 2500 rpm. Then, 20 mL of hexane was added to the glass flask and the stirring was maintained for 2 h. After turning off agitation, it was observer phase separation and solid material remained adsorbed at liquid-liquid interface as a thin film. For deposition, a glass rod with "L" shape was added to a 50 mL Beaker with glass and silicon substrates positioned on top of the rod base. 20 mL of deionized water was added to cover the substrates and about 3 mL of hexane was added to form a liquid-liquid interface inside the Beaker. The thin film adsorbed at the liquid-liquid interface in the round-bottom flask was transferred with a plastic pipette to the Beaker by collecting the thin film at the interface and adding slowly at the interface of the Beaker. Water and hexane from Beaker were constantly removed to maintain the volumes approximately constants. After most of the interfacial thin film has been transferred, most of the superior phase was removed from the 50 mL Beaker with pipette and then the glass rod containing substrates was moved vertically and slowly. Thin films fresh deposited were dried at ambient conditions for 30 min and then dried in an oven at 343 K for 30 min and at 373 K for 2 h. Thin films were maned according the aqueous dispersion used followed by "/hexane", for example MWCNT-H_2O/hexane for the interfacial thin film prepared with MWCNT-H_2O dispersion. Thin films with more than one deposition were prepared following the procedure described above, but using a glass substrate that already contains deposited materials instead of clean glass substrate

Gas chromatography-mass spectrometry (GC-MS) analysis were conducted in an analyzer from Shimadzu, model GCMS-QP2010 Ultra with capillary column RTX-5 from J&W Scientific (30 m x 0.25 mm x 0.25 µm). Gas chromatograms were performed with temperature range from 323 K to 523 K (10 K min^{-1}) and using He as mobile phase (1 mL min^{-1}). Injector temperature was settled at 523 K, interface temperature at 523 K and ions source at 473 K. Mass spectrometry was performed in scan mode, with electron ionization at 70 eV, and m/z ratio was monitored between 40 to 500. It was performed two separated GC-MS analysis for each sample, one starting at 3.5 min after sample injection with split rate equal to 30 to eliminate solvent and to detect only BHT, and another analysis starting at 12 min after sample injection in splitless mode to detect other compounds than BHT. It was injected 1 µm of sample for each GC-MS analysis.

UV-Vis spectra were acquired in a Shimadzu equipment, model UV-2450, from 200 to 900 nm, with 0.5 nm of resolution and using air as absorbance blank. Spectra of aqueous dispersions were acquired in quartz cuvette with optical path of 1 mm and spectra of thin films were acquired direct from samples deposited over glass substrates.

Photoluminescence spectra were acquired in a Horiba fluorimeter, model Fluorolog with aqueous dispersions in quartz cuvette or thin films deposited over quartz substrates. Sample SWCNT-A-H_2O was excited at 582 nm and sample SWCNT-H-H_2O was excited at 457 nm. BHT-H_2O-B sample was excited at 314 and 725 nm. All spectra were recorded starting from 20 nm after excitation wavelength to 900 nm and excitation wavelengths were chosen based on absorption bands from UV-vis spectra.

Raman spectra were acquired in a Renishaw Raman image spectrometer, coupled to an Olympus optical microscope, operating with Ar^+ laser or He-Ne laser. Raman spectrum of solid MWCNT were collected with Ar^+ laser, between 2000 and 1000 cm^{-1}, with 20 accumulations of 30 s and objective lens of 50x. Raman spectra of SWCNT-A and SWCNT-H were collected with Ar^+ and He-Ne lasers, between 4000 and 130 cm^{-1}, with 2 accumulations of 10 s and objective lens of 50x.

Zeta potentials were measured using a Malvern equipment, model ZetaSizer Nano S, at 298 K using Smoluchowski model Measurements were conducted in triplicate for each sample and it was done 20 scans for each measure.

Dynamic light scattering was measured in a particle size analyzer Microtrac, model Nanotrac 150. Analysis were conducted in triplicate performing 5 scans per measure.

Measurements of sheet resistance were performed with a four probe Jandel universal probe equipment, with 1.0 mm between each probe. Four probe analysis were conducted with thin films deposited over glass substrates, applying 10 mN on each probe and using electrical current of 1 μA. It was conducted seven measurements for each deposition of each thin film and the results ae expressed as the medium values.

Scanning Electronic Microscopy (SEM) was performed on a Tescan microscope, model MIRA3 FEG-SEM, operating with 10 kV and work distance of 5 mm. Images were collected using an In-beam detector of Secondary Electrons (SE). Thin films deposited over silicon substrates was fixed on stub with carbon adhesive and electrical contact was made with copper adhesive between substrate and stub.

Equation S1[7]

$$CCC\ (mmol\ L^{-1}) = \frac{9.85^{x}10^{4}\varepsilon^{3}\varepsilon_{0}^{3}k_{B}^{5}T^{5}}{N_{A}e^{6}z^{6}A^{2}} tanh^{4}\left(\frac{ze\psi_{\delta}}{4k_{B}T}\right)$$

Equation S1 provides CCC values in mmol L^{-1} as shown and furnish the minimum electrolyte concentration to coagulate a lyophobic dispersion; ε is water relative permittivity (80.1), ε_0 is the vacuum electric permittivity ($8.854^{x}10^{-12}$ C V^{-1} m^{-1}), k_B is Boltzmann constant ($1.381^{x}10^{-23}$ J K^{-1}), T is absolute temperature, N_A is the Avogadro number ($6.022^{x}10^{23}$ mol^{-1}), e is elementary charge ($1.602^{x}10^{-19}$ C), z is the counterion valence, A is Hamaker constant, ψ_δ is electric potential at Stern layer that was considered equal to zeta potential (-31 mV for MWCNT-H_2O). Combining the CCC value equal to 1 mmol L^{-1}, with the zeta potential value, Equation S1 provides a Hamaker constant equal to $1.73^{x}10^{-19}$ J for MWCNT-H_2O sample. This value of Hamaker constant was used for the calculations for both SWCNT dispersions.

Equation S2[7]

$$U_T = \frac{-A}{12}\left[\frac{1}{x(x+2)} + \frac{1}{(x+1)^2} + 2ln\left(\frac{x(x+2)}{(x+1)^2}\right)\right] + \frac{32\pi a\varepsilon\varepsilon_0 k_B^2 T^2}{z^2 e^2}\tanh\left(\frac{ze\psi_\delta}{4k_B T}\right)exp(-\kappa D)$$

The first term of Equation S2 is the attraction (U_A) contribution to the interaction potential, which is negative because contributes to decreases the total Gibbs energy of the system, and the second is the repulsion term (U_R) that is positive because it contributes to preserve dispersion stability and, then, to maintain higher values of total area per volume unit.[7] The variable x is equal to $D/2a$, D is the distance between two particles, a is particle radius, π is number Pi (3.141593), and κ is the inverse of Debye length. For the calculation of κ value, ionic concentration was estimated as 0.1 mmol L^{-1} for the three dispersions and κ calculated considering a monovalent symmetric electrolyte. DLS of anisotropic particles furnish the hydrodynamic radius, that relates the diameter and the length of carbon nanotubes.[8] Particle radius (a) of MWCNT-H_2O, SWCNT-A-H_2O and SWCNT-H-H_2O dispersions were estimated as 50, 61 and 89 nm by DLS measurements respectively (half of the hydrodynamic size).

Optimization of the BHT concentration in THF solution

Since BHT are very poorly soluble in water, there is an maximum concentration of BHT in THF that will not precipitate after water addition. High concentrations of BHT as 1×10^{-2} or 1×10^{-1} mol L^{-1} can be used to prepare stable and concentrated organic dispersions of carbon nanotubes in THF, but the BHT immediately precipitate when water is mixed to these highly concentrated BHT/THF solutions, resulting in a white and milky dispersion of BHT with macroscopic black aggregates of carbon nanotubes. The optimal concentration of BHT in THF to avoid the precipitation and achieve stable aqueous dispersions is between 1×10^{-4} and 1×10^{-3} mol L^{-1}, which has been used in our experimental procedure (5×10^{-4} mol L^{-1} for MWCNT and 1×10^{-3} mol L^{-1} for SWCNT). The same tendency is observed for MWCNT, as can be seen in Figure S1. Both diluted and concentrated BHT solutions prepared in distilled THF can disperse carbon nanotubes, however when concentrated BHT solutions were used they induce precipitation of both carbon nanotubes and BHT after water addition as shown in the pictures from Figure S1.

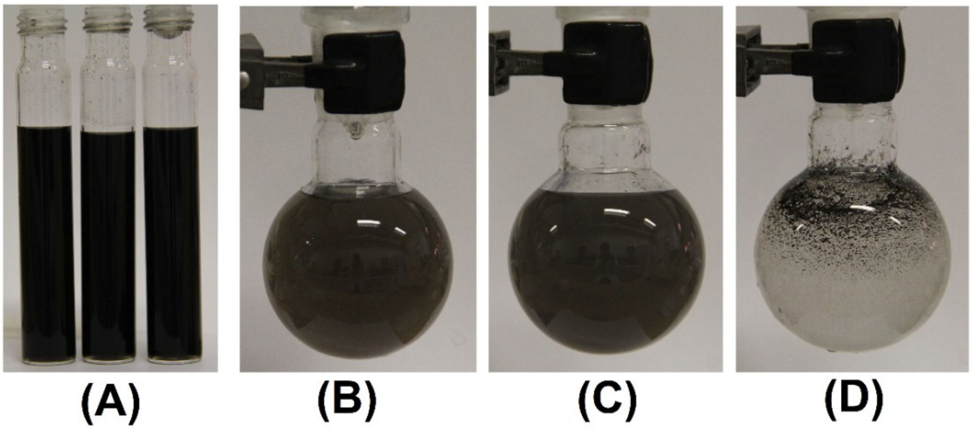

Figure S1. Pictures of MWCNT dispersions prepared with BHT solutions in distilled THF with different concentrations by sonicating 0.5 mg of MWCNT and 10 mL of BHT solution during 1 h in bath cooled with small portions of ice: BHT concentrations equal to $1^{x}10^{-3}$, $1^{x}10^{-2}$ and $1^{x}10^{-1}$ mol L^{-1} from left to right (A); Pictures of MWCNT dispersed in BHT solutions after addition of 100 mL of deionized water: BHT $1^{x}10^{-3}$ mol L^{-1} (B), BHT $1^{x}10^{-2}$ mol L^{-1} (C), and BHT $1^{x}10^{-1}$ mol L^{-1} (D); Pictures (C) and (D) have aggregates of carbon nanotubes at the liquid-air interface (C) or suspended in liquid phase (D). Pictures were obtained just after sonication or after water addition.

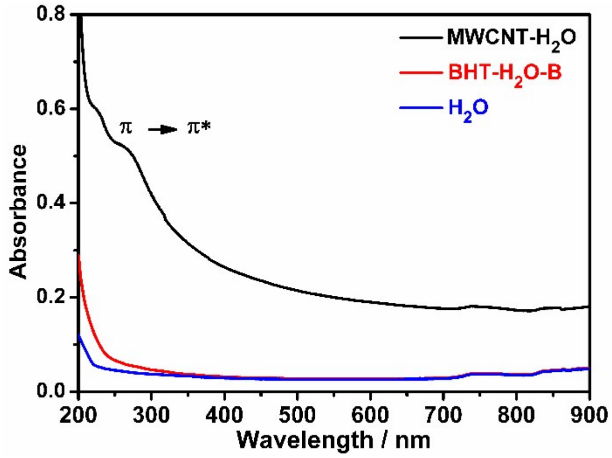

Figure S2. UV-Vis spectra of MWCNT-H_2O dispersion, BHT-H_2O-B solution and deionized water. Bands at 270 nm and around 750 nm are referent to BHT and water, respectively.

Discussion about Mass Spectrometry (MS) and fragmentation profiles of BHT and its dimer

Mass spectrometry was performed for ethyl ether extracts with concentrated MWCNT dispersions (5,0 mg) prepared in THF solution of BHT (50 mL of $1^{\times}10^{-2}$ mol L^{-1} solution) and with blank sample prepared exactly as the same without nanotubes. It was performed two analysis in split mode and two in splitless mode with each sample.

Analysis with split mode of both samples detected 2,6-di-tert-butyl-4-methylphenol (BHT) and its mass spectrum is shown in Figure S3 (A) and it is identical to previously reported in literature[9,10]. The molecular ion is detected at m/z equal to 220 ($[M]^+$) and the base peak is at 205 that is referent to molecular ion minus methyl fragment ($[M\text{-}CH_3]^+$). The peak at 177 is referent to 205 fragment with loss of an additional CO ($[M\text{-}C_2H_3O]^+$), which is typical of phenolic compounds. Signal at 161 is referent to 177 fragment with loss of methyl and proton and fragment at 145 is referent to 161 with loss of methyl and proton. The fragment at 105 is referent to BHT with loss of one proton and two terc-butyl groups and fragment 57 is referent to terc-butyl group.

Analysis with splitless mode detected 1,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)-ethane (the BHT dimer) only for sample prepared with MWCNT, which obtained by BHT oxidative dimerization. Its mass spectrum is presented in Figure S3 (B), and it is identical to the previously reported in literature[9,10]. The molecular ion is detected at m/z equal to 438 ($[M]^+$) and the base peak is at 219, which is referent to cleave of the central ethyl group ($[M-C_{15}H_{23}O]^+$). Signal at 203 is referent to 219 fragment with loss of methyl and proton ($[M-C_{14}H_{19}O]^+$) and fragment at 57 is referent to terc-butyl group.

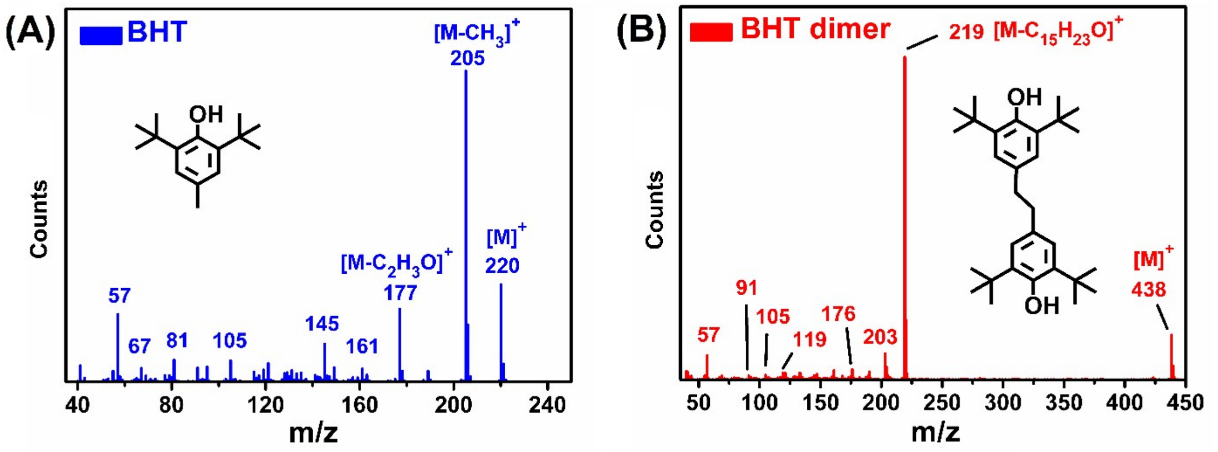

Figure S3. Mass spectra of 2,6-di-tert-butyl-4-methylphenol (BHT) (A) and 1,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)-ethane (BHT dimer) (B) with attributions of the principal signals and with the respective structural representation inserted in each spectrum. The fragmentation profiles of both compounds are in accordance with literature[9,10].

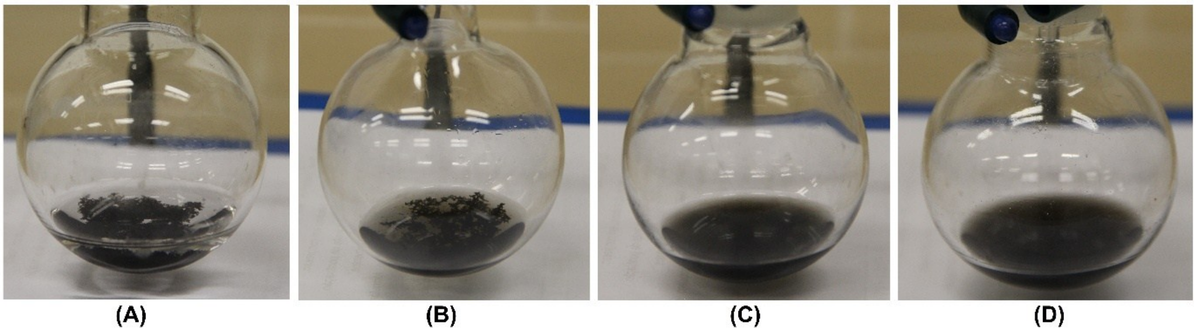

Figure S4. Pictures of MWCNT sonicated in distilled THF (A), phenol solution ($1^{x}10^{-3}$ mol L^{-1}) (B), BHT solution ($1^{x}10^{-3}$ mol L^{-1}) (C), and hydroquinone solution ($1^{x}10^{-3}$ mol L^{-1}) (D); All phenolic solutions were prepared with distilled THF and samples were prepared with 0.5 mg of MWCNT and 10 mL of the respective phenolic solution sonicated during 1 h in bath cooled with small portions of ice. Pictures were obtained 12 h after sonication.

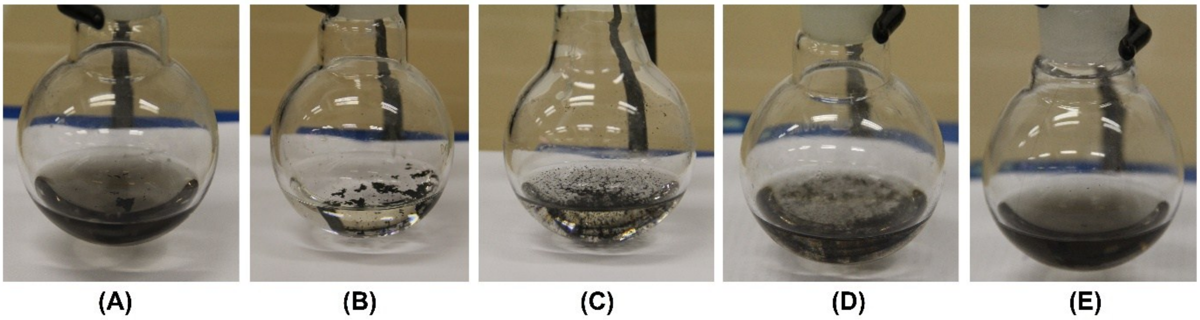

Figure S5. Pictures of MWCNT sonicated with BHT solution ($1^{x}10^{-3}$ mol L^{-1}) prepared with ethanol (A), ethyl ether (B), acetonitrile (C), toluene (D), and acetone (E); All samples were prepared with 0.2 mg of 0.5 mg MWCNT and 20 mL of BHT solution in the respective solvent and sonicated during 30 min in bath cooled with small portions of ice. Pictures were obtained 12 h after sonication.

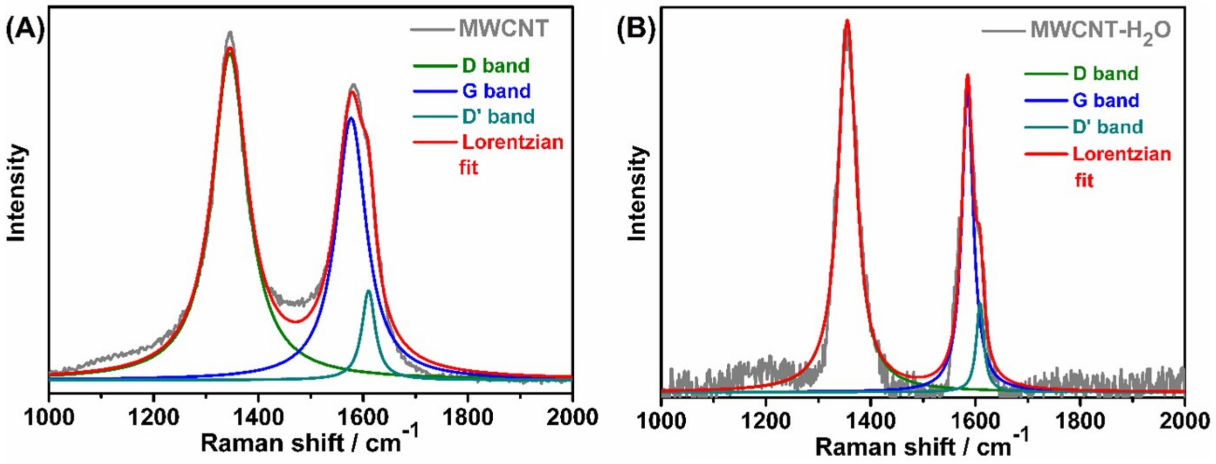

Figure S6. Raman spectra with the respective Lorentzian fits of MWCNT (A) and MWCNT-H_2O samples (B).

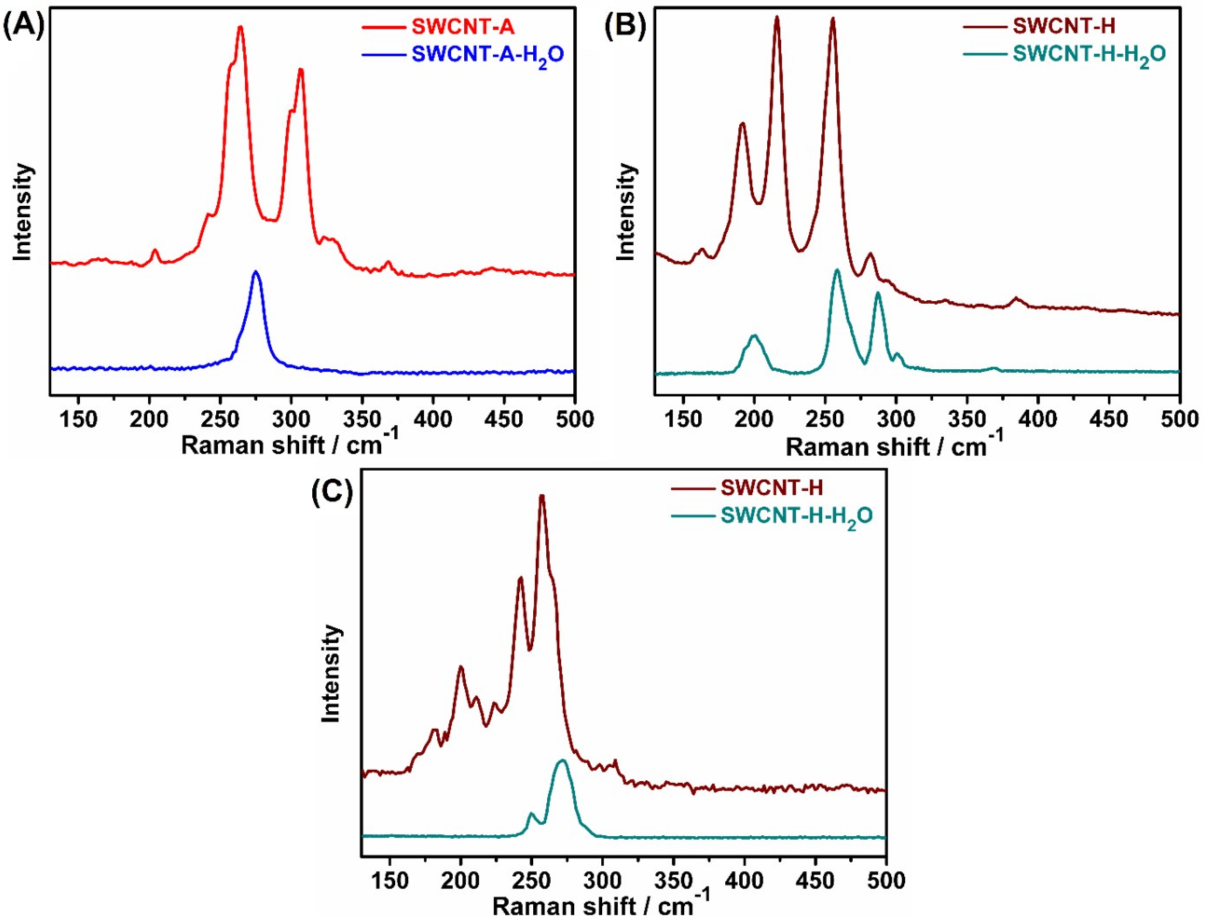

Figure S7. Raman spectra of SWCNT-A and SWCNT-A-H_2O samples acquired with green laser (A); Raman spectra of SWCNT-H and SWCNT-H-H_2O samples acquired with red laser (B) and green laser (C). All dispersions spectra shown were obtained after subtracting water spectrum.

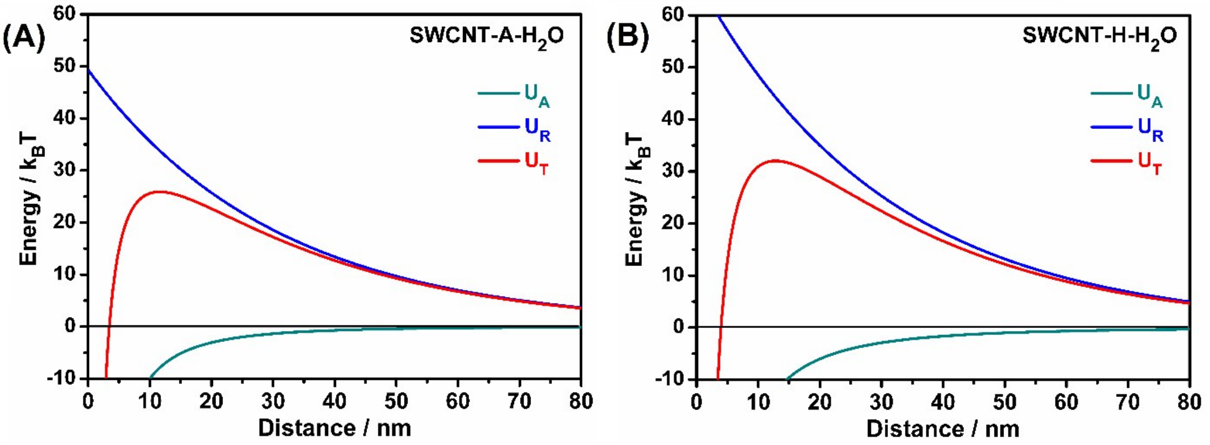

Figure S8. Graphics of total interaction energy (U_T), attraction energy (U_A) and repulsion energy (U_R) of two particles as a function of distance calculated using physical properties of SWCNT-A-H_2O (A) and SWCNT-H-H_2O (B) dispersions.

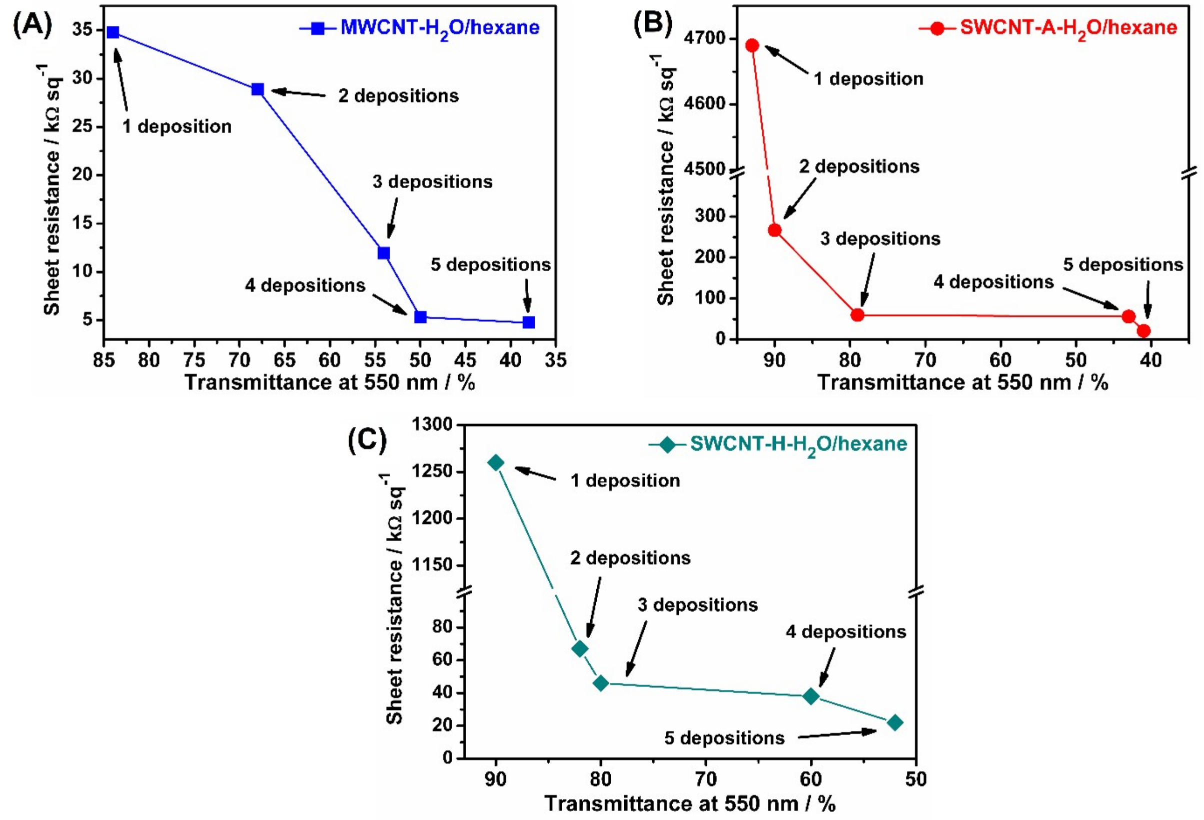

Figure S9. Sheet resistance against transmittance value at 550 nm for MWCNT-H_2O/hexane (A), SWCNT-A-H_2O/hexane (B), and SWCNT-H-H_2O/hexane (C) thin films deposited over glass substrates; Each point represents a thin film with one to five depositions according internal legend.

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