Electronic Supplementary Material

Formation of trihalomethanes and haloacetic acids during chlorination of functionalized carbon nanotubes

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Reagents. All reagents were ACS grade or higher. Anhydrous sodium sulfite (Fisher Chemical; ACS grade) was used to quench chlorine during sample preparation. Anhydrous sodium phosphate dibasic (RPI; >99%) was used to buffer pH in aqueous solutions. Disodium ethylenediamine tetraacetic acid dehydrate (EDTA; Sigma; ACS reagent), ferrous ammonium sulfate hexahydrate (FAS; J.T. Baker; ACS grade), N,N-diethyl-p-phenylenediamine (DPD; Aldrich; 97% purity), and sulfuric acid (Fisher; ACS Plus) were used in the colorimetric titration method for analysis of chlorine. Pentane (n-pentane; Fisher; HPLC grade) was used for liquid-liquid extraction of THMs. 1,2-dibromopropane in methanol (Crescent Chemical Co., Inc.), and THM4 and HAA6 standard in methanol (Supelco; analytical standard) were used for GC standards for method calibration. Sodium sulfate anhydrous (Fisher; ACS grade) and methanol (Fisher; Optima grade) were used for HAA extraction. Nitric acid (Sigma-Aldrich; ACS reagent) was used for functionalization of CNTs. m-Aminobenzenesulfonic acid (ABS; Aldrich; 97%), aniline (Sigma-Aldrich; ACS reagent), and ammonium persulfate (Sigma-Aldrich; ACS reagent) were used to synthesized PABS. All solutions were prepared in deionized water using a Thermo Scientific Barnstead TII.

Surface oxidation of select commercial carbon nanotubes. CNTs oxidized with nitric acid (HNO_3; denoted hereafter with an “-N” following the CNT name) were produced by suspending 100 mg of as-received CH MWNF or NL SWNF in 250 mL of concentrated HNO_3.[1-4] The suspension was sonicated (Bransonic Ultrasonics Corporation, 151OR-DTH, 42 kHz ± 6%) for 1 h prior to refluxing the mixture at 140 °C for 1.5 h while stirring vigorously. CNTs oxidized with a mixture of sulfuric acid (H_2SO_4) and HNO_3 (denoted by “-S/N”) used a suspension of 100 mg of as-received CNTs in 8 mL of concentrated 3:1 H_2SO_4:HNO_3.[5, 6] The suspension was then dispersed using sonication for 1 h, and the mixture was subsequently refluxed at 70 °C for 8 h without stirring. For both methods, the oxidized CNTs were allowed to cool overnight before filtering the suspension with a 0.22 µm polycarbonate filter (EMD Millipore). The filtered solids were cleaned by repeated washing with DI water until the filtrate exhibited a pH greater than 5, at which point the oxidized CNTs were allowed to dry overnight at 100 °C. The resulting powder was then pulverized with a mortar and pestle before use.

Preparation of polymers. Experiments were conducted with PABS and PEG in the absence of CNTs so that the DBP formation of native polymers could be compared to that measured for polymer-functionalized CNTs. PEG (600 Mn) was purchased from various manufacturers (Aldrich, Alfa Aesar, and Sigma (Bio Ultra)) and used as received. Because reactivity of PEG was consistent across all manufacturers, only PEG from Aldrich was used for the experiments described in the main text.

PABS was not commercially available, but instead was synthesized from established methods.[7, 8] PABS was prepared by mixing ABS and aniline (20 mol% of ABS) in 1 M HCl with ammonium persulfate (10:1 molar ratio to ABS). The mixture was allowed to react in an ice bath (~4 °C) for 6 h, after which the solution was filtered with a 0.22 µm polycarbonate filter. The precipitate was washed with acetone then suspended in water before finally precipitating it again in acetone. The precipitate was collected via filtration and allowed to dry at room temperature. The product was confirmed as PABS via UV spectroscopy in 1 N NaOH solution, which yielded the expected absorbance bands at ~290 nm and ~510 nm diagnostic of PABS (see Figure S10).[8] Polymers were then suspended in DI water at 1 g/L and sonicated for an hour before use.

Analytical methods. For titrations to determine HOCl and monochloramine concentrations, 5 mL of each buffer reagent and the DPD indicator solution were added to 100 mL of diluted sample, with the solution turning pink to red in hue in the presence of free chlorine. The free chlorine concentration was then quantified by titration with ferrous ammonium sulfate (FAS) until the red color disappeared. Monochloramine was quantified by adding potassium iodide crystals to the titration flask after titrating for free chlorine to produce the same color hue which was again titrated to clear with FAS.

THMs were analyzed according to EPA Method 551.1, which relied upon quantification with gas chromatography (GC) coupled with an electron capture detector (ECD) after liquid-liquid extraction while using 1,2-dibromopropane as an internal standard. Briefly, pentane (2 mL) containing 30 µg/L of 1,2-dibromopropane internal standard was added to 15 mL of sulfite quenched sample and vigorously mixed for 10 s. The pentane layer was collected after the phases separated (~1 min). The contents of pentane were injected (3 µL; in split-less mode) into an HP 6890N gas chromatograph (GC; Agilent Technologies, Inc.) housing a DB-5 column (J&W 122-5033) leading into an electron capture detector (ECD; Agilent Technologies, Inc.; G2397A). The temperature program was as follow: hold 40 °C for 5 min; ramp 40 to 70 °C at 10 °C/min; ramp 70 to 260 °C at 20 °C/min. The injector temperature was 200 °C. Helium was used as the carrier gas at 1 mL/minute (constant flow). The ECD was set at 250 °C. A method detection limit of 0.5 µg/L was determined.

Haloacetic acid samples were analyzed according to EPA Method 552.3, which uses GC-ECD after derivatization and liquid-liquid microextraction. Briefly, 1.75 mL of concentrated sulfuric acid was added to 35 mL of sample volume to bring the pH of the sample down to less than 0.5. Next, 14 grams of sodium sulfate anhydrous (Na_2SO_4) and 1.75 grams of copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) was added to the sample and shaken until dissolved. Then 4 mL of methyl tert-butyl ether (MTBE) and 20 µL of 5 µg/L internal standard, 1,2-dibromopropane, were added to the solution. Solutions were vigorously mixed for 1 min. The solutions were then methylated by transferring 3 mL of the upper MTBE layer into a 15 mL amber vial with PTFE-lined screw caps, adding 2 mL of 10% sulfuric acid in methanol, and reacting them for 2 h in a 50 °C water bath. Vials were removed from the water bath and allowed to cool. Then 5 mL of 10% sodium sulfate solution was added to each vial and shaken by hand for 2 min. The mixture was allowed to settle (~ 1 min) and 1 mL of the upper MTBE layer was collected for GC-ECD analysis. The sample was injected into the GC in split-less mode and separated on a DB-5 column. The temperature program was as follows: hold 35 °C for 10 min; ramp 35 to 75 °C at 5 °C/minute; hold 75 °C for 15 min; ramp 75 to 100 °C at 5 °C/minute; hold 100 °C for 5 min; ramp 100 to 135 °C at 5 °C/minute; and hold 135 °C for 5 min. The injector temperature was set at 250 °C. Helium was used as the carrier gas at 1 mL/minute (constant flow). The ECD was set at 250 °C. A method detection limit of 3 µg/L for MCAA, 1 µg/L for DCAA, 1 µg/L for TCAA was determined.

Characterization of CNTs and CNT suspensions. The morphology of reacted and unreacted CNT samples were examined with transmission electron microscopy (TEM). TEM images were collected on a JEOL JEM 1230 transmission electron microscope operating in bright field mode at 120 kV. TEM samples were prepared by dip-coating a carbon Cu grid in sample suspension. For XPS analysis, the X-ray gun was operated using a 15 mA emission current at an accelerating voltage of 15 kV. Low-energy electrons were used for charge compensation to neutralize the sample. High-resolution spectra were acquired in the region of interest using the following experimental parameters: 20–40 eV energy window; pass energy of 20 eV; step size of 0.1 eV, and dwell time of 1000 ms. The absolute energy scale was calibrated to the Cu 2p2/3 peak binding energy of 932.6 eV using an etched copper plate. All spectra were calibrated using the C 1s peak at 285.0 eV. CasaXPS software was used to process the XPS data.

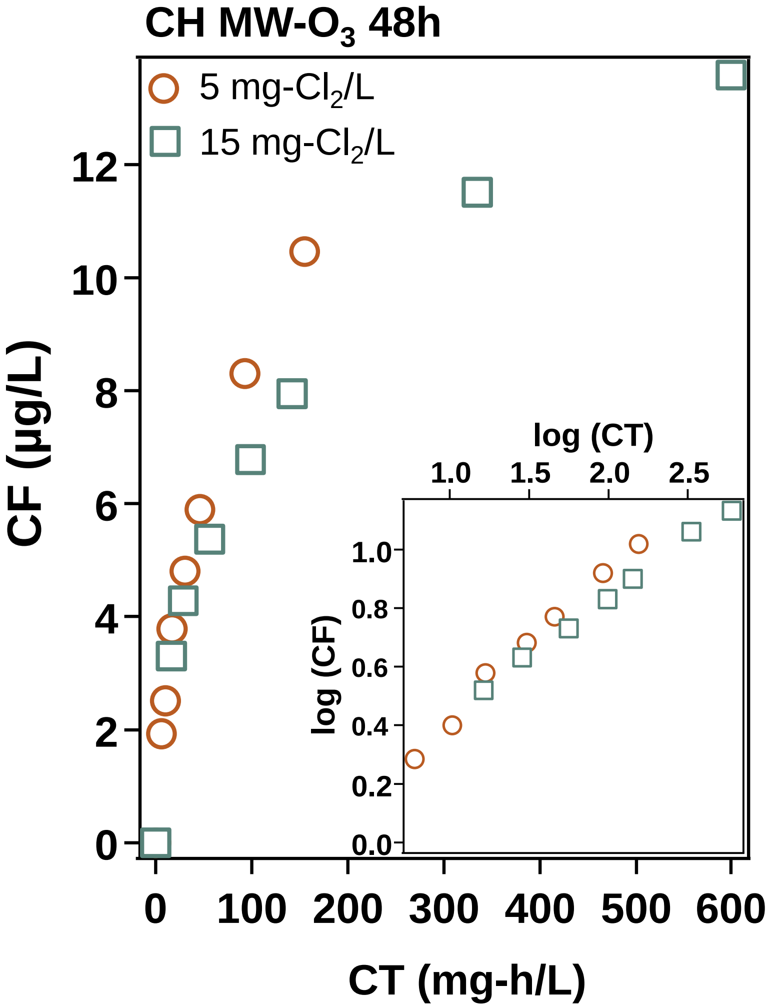

Figure S1: CF formed as a function of CT for CH MW-O_3 48h reacted with 5 and 15 mg-Cl_2/L initial HOCl. Generally, CF formation was independent of initial chlorine concentration across CT values explored, particularly lower CT values, which are most representative of water and wastewater treatment. Insert shows the data on a log-log scale. Experimental conditions: 10 mg/L CNT, 5 mM phosphate buffer at pH 8, 0-48 h reaction.

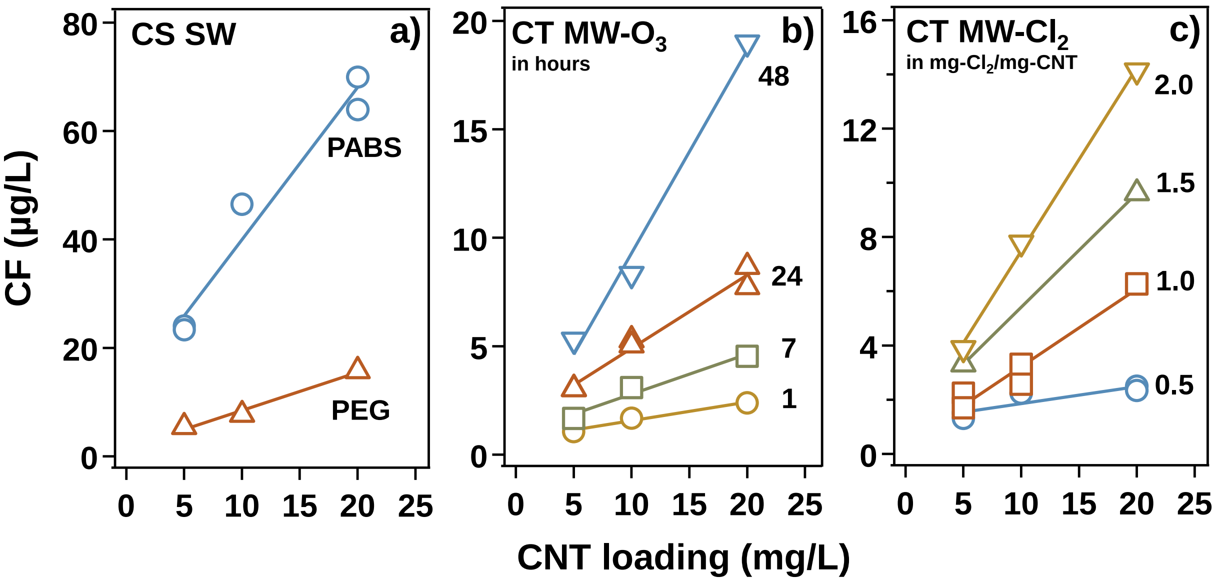

Figure S2: CF formation as a function of CNT concentration (in mg/L) for (a) polymer functionalized, (b) ozone oxidized, and (c) chorine oxidized CNTs during reaction with chlorine. As is expected for a surface-mediated process, CF formation increased linearly with CNT loading. Linear regression fits with an R^2 of at least 0.8 are displayed with the data. Experimental conditions: 15 mg-Cl_2/L initial HOCl, 5 mM phosphate buffer at pH 8, and 4 reaction.

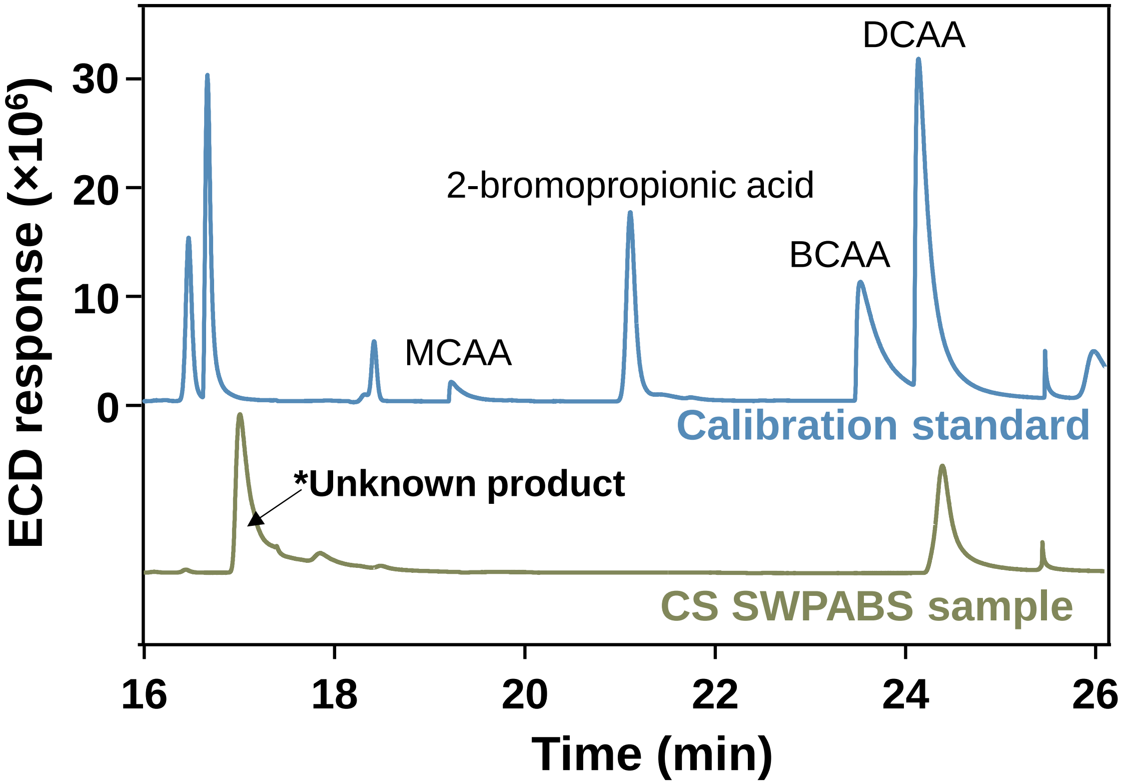

Figure S3: GC-ECD chromatogram of a chlorination sample taken from a suspension of CS SWPABS (green). The sample chromatogram is compared to that of HAAs standard (blue; MCAA t_R = 19.2, BCAA t_R = 23.51, DCAA t_R = 24.13 in min). The peak at 16.97 min in the CS SWPABS sample is an as yet unidentified chlorination byproduct. Experimental conditions of sample: 10 mg/L CNT, 15 mg-Cl_2/L initial HOCl, 5 mM phosphate buffer at pH 8, and 1 h reaction.

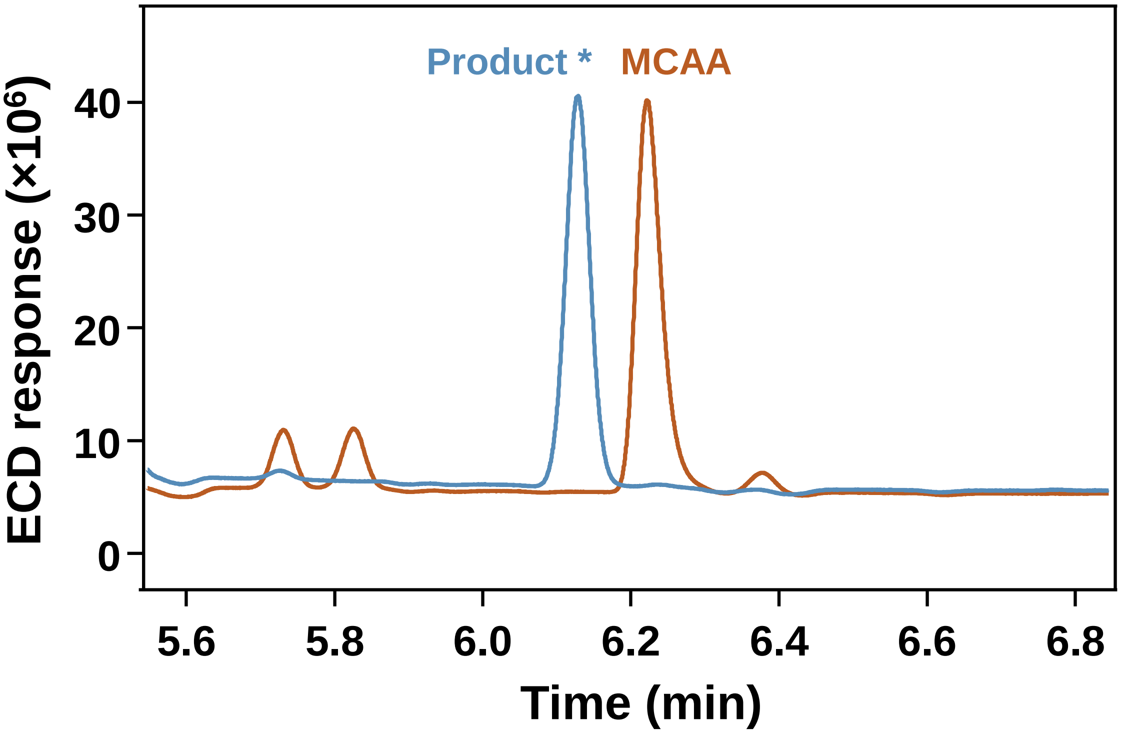

Figure S4: GC-ECD chromatogram of an as yet unidentified byproduct formed during chlorination of CS SWCOOH (blue; t_R = 6.13 min) compared with that of a MCAA standard (orange; t_R = 6.21 min). Experimental conditions of sample: 10 mg/L CNT, 15 mg-Cl_2/L initial HOCl, pH 8, 24 h reaction. A DB-5.625 GC column was used to resolve the difference between the product peak and MCAA.

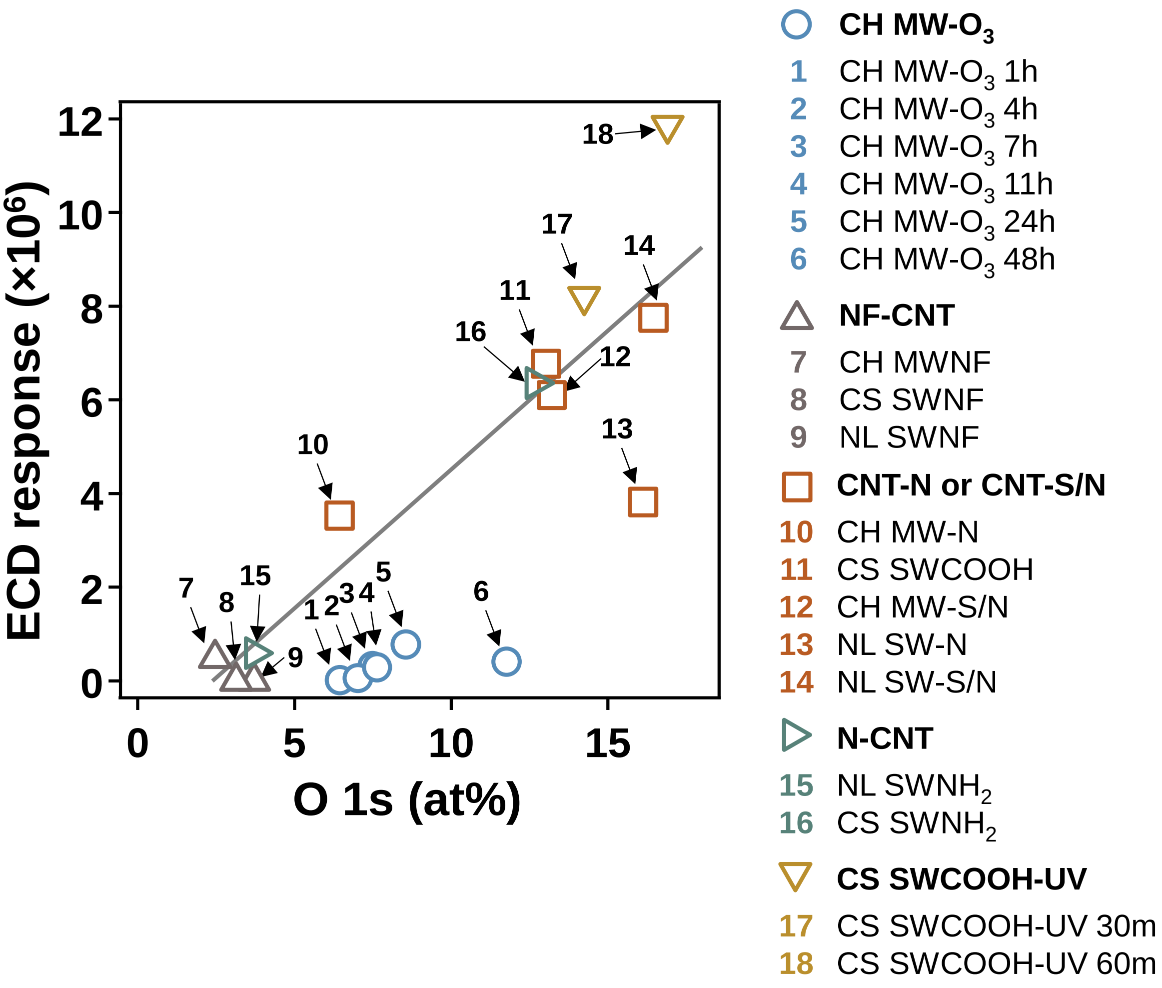

Figure S5: ECD response of the as yet unidentified byproduct (t_R = 6.213 min in Figure S3) versus the CNT surface oxygen concentration quantified via the O 1s region of XPS. Experimental conditions: 15 mg-Cl_2/L initial HOCl, 10 mg/L CNT, 4 h reaction, and 5 mM phosphate buffer at pH 8. Linear regression through all data except CH MW-O3 is shown (R^2 = 0.793).

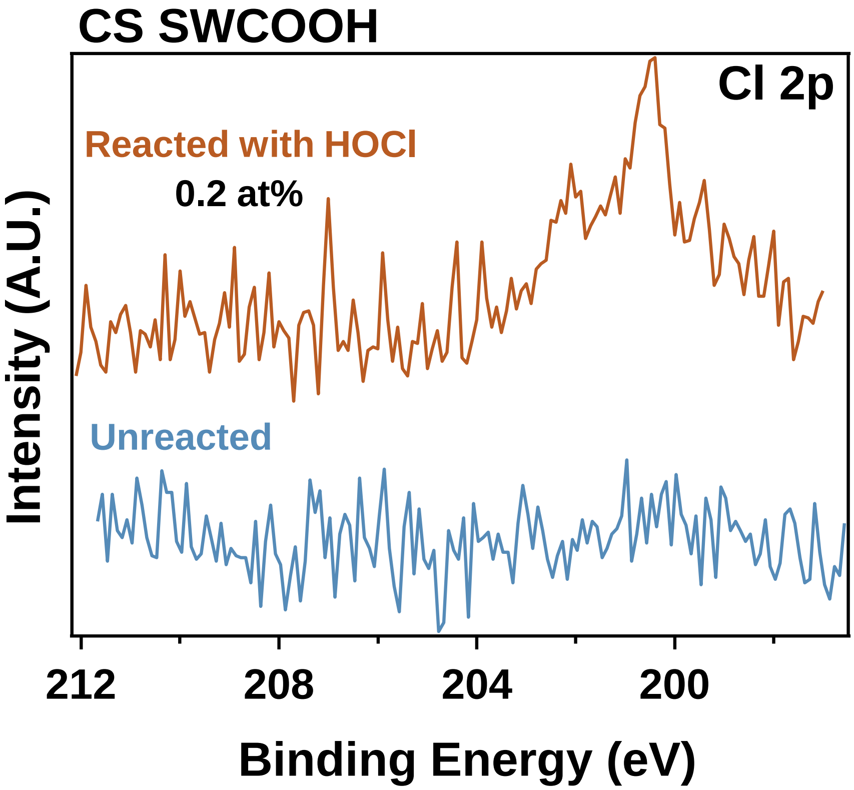

Figure S6: XPS spectra of CS SWCOOH comparing the Cl 2p regions before (blue) and after (orange) reaction with HOCl. Experimental conditions: 15 mg-Cl_2/L initial HOCl, 10 mg/L CNT, 5 mM phosphate buffer at pH 8, and 4 h reaction.

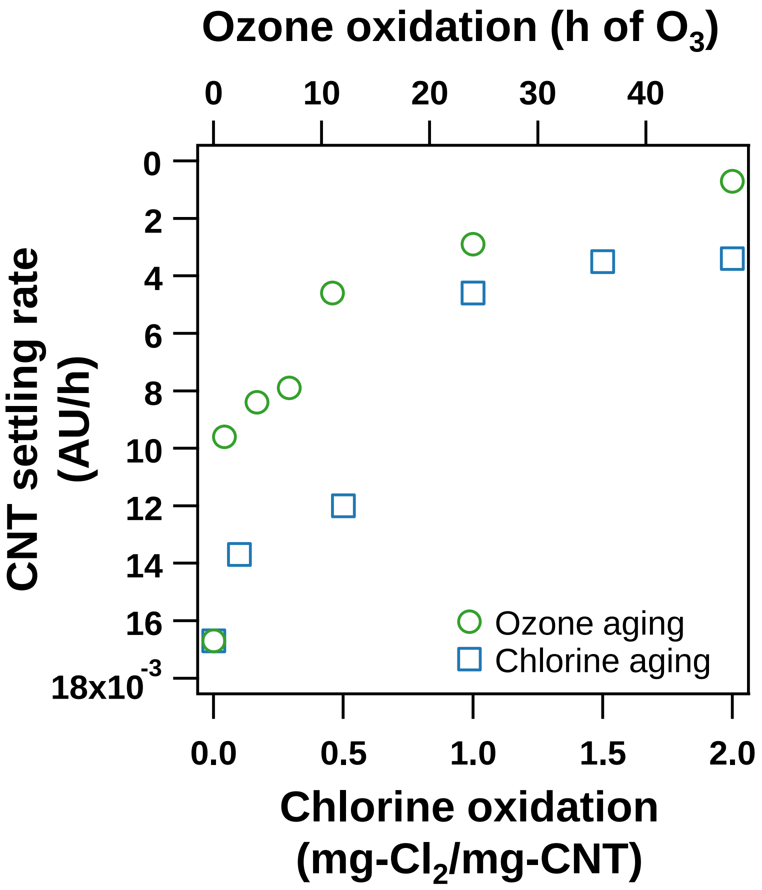

Figure S7: Settling rates of CNTs in DI water (with no additional ionic strength) as a function of their extent of oxidation with either ozone (green circles; top x-axis) or chlorine (blue squares; bottom x-axis). Settling rates, in absorbance units (AU) per hour (h), were calculated via a linear regression through the 5-20 min linear region of plots of absorbance over time, where a smaller setting rate indicates better suspension stability. Sedimentation studies were conducted using a 1 cm path length cuvette, with absorbance measured at a wavelength of 700 nm. Experimental conditions: 1 g/L CH MWNF in DI; chlorination at the concentration indicated or continuous ozonation (19.2 mg/L steady-state concentration) for the time indicated.

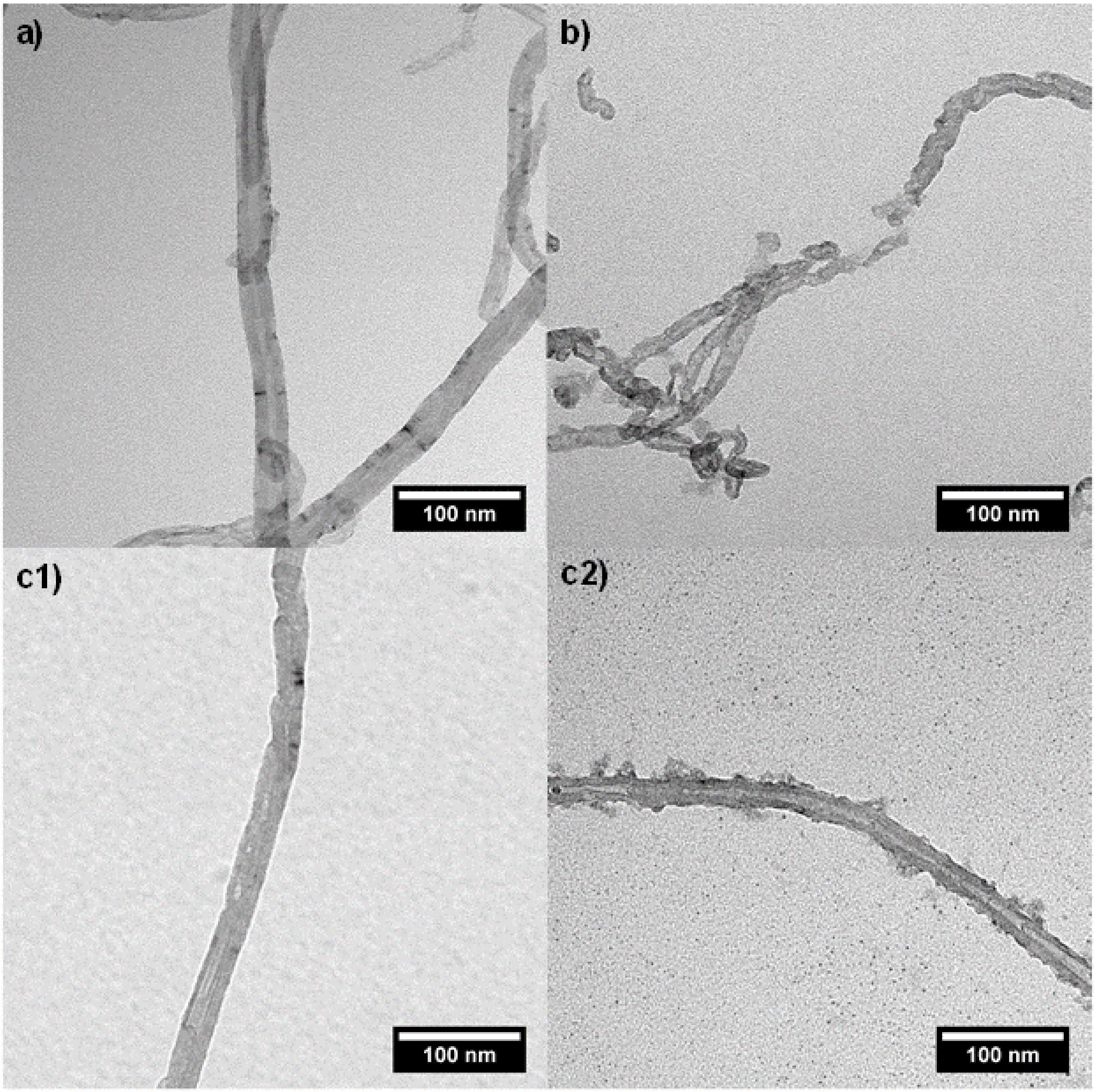

Figure S8: TEM images of (a) CH MWNF, (b) CH MW-O_3 48h, and (c1) and (c2) CH MW-Cl_2 1.0 mg/mg-CNT, illustrating extent of structural changes induced by CNT oxidation. Panel (b) depicts fragmentation of CNTs by extended ozone treatment, behavior consistent with studies that have explored CNT surface oxidation via ozone. Panels (c1) and (c2) were collected from the same chlorine-processed sample but imaged at different spots on the TEM grid, suggesting variability in the extent of surface processing for CNTs in suspension. Specifically, the CNT in panel (c1) appears practically indistinguishable from unreacted CNT, whereas panel (c2) suggests evidence of surface residue (potentially amorphous carbon) generated via the chlorination reaction.

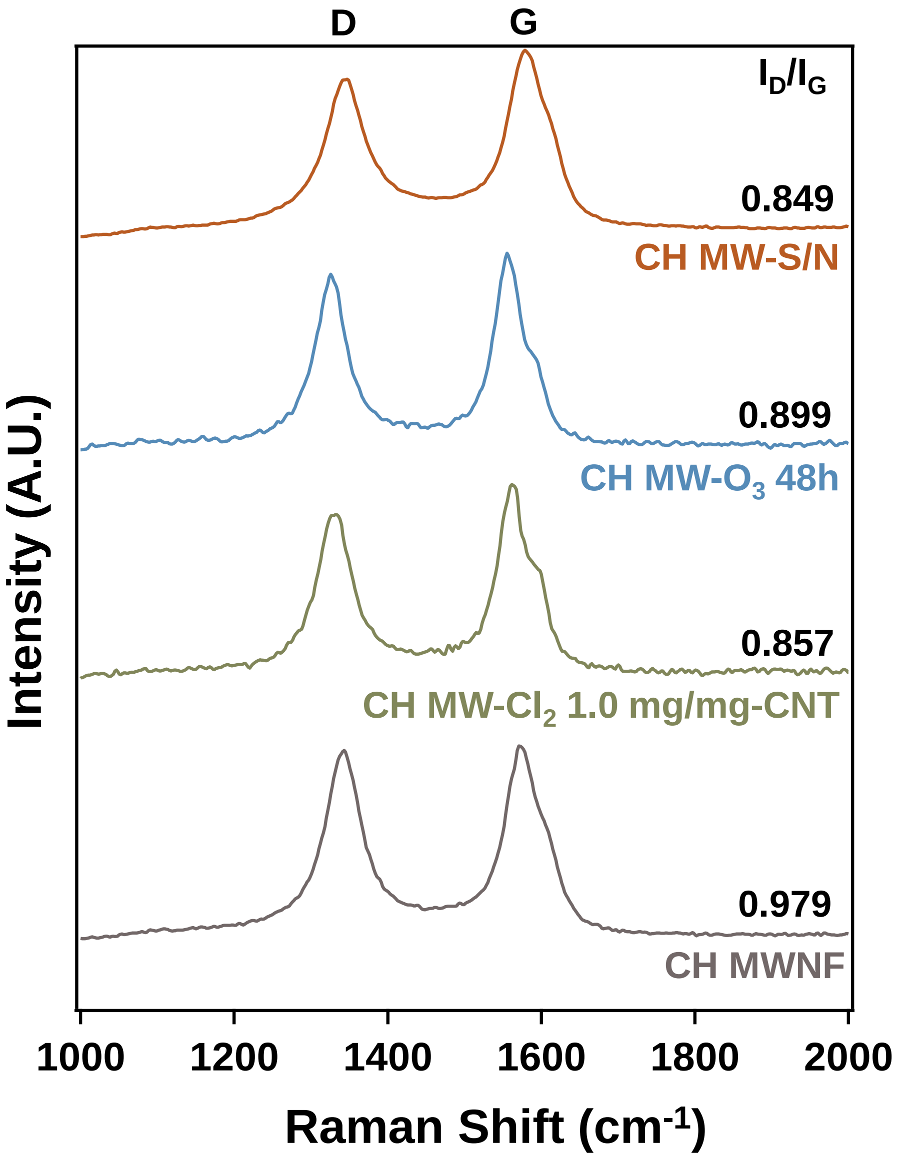

Figure S9: Raman spectra of CH MWCNTs treated with chlorine (1.0 mg-Cl_2/mg-CNT), ozone (48 h) and acid (mixture of sulfuric and nitric acid; S/N). The I_D/I_G band ratios determined from Raman are included.

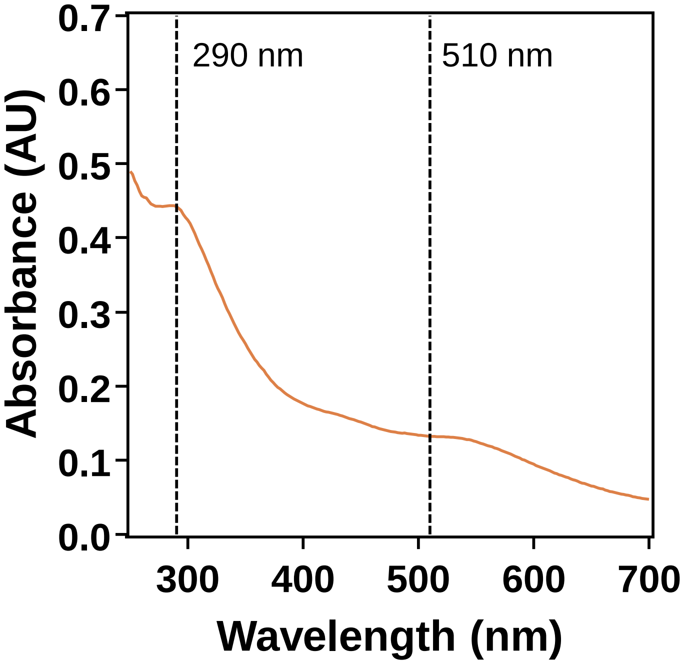

Figure S10: UV-vis absorbance scan of synthesized PABS in 1 N NaOH solution, analyzed using a 1 cm path length quartz cuvette. Dashed lines represent diagnostic absorbance bands at 290 nm and 510 nm expected for PABS.

References

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