Transformations of Oxidized Multiwalled Carbon Nanotubes Exposed to UVC (254nm) Irradiation

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Supporting Information

Buffer Selection

Choosing suitable buffer that maintains the pH during O-MWCNT irradiation experiments without degrading or influencing the transformation process was key in obtaining reproducible and reliable results. We avoided the use of buffers that contained conjugated ring structures because those could be degraded by the UVC light, and we avoided the use of buffers that could potentially produce electrons or reactive oxygen species that could influence the transformation of O-MWCNTs in suspension. The buffer needed to be polyprotic so it could be used over the range of pH values (4 – 10) we wished to study. Although carbonate has been used in previous experiments with O-MWCNTs,[1-3] it was considered potentially unstable due to the potential for CO_2 evolution. Therefore, we chose phosphate as the buffer for our experiments because it allowed buffered solutions to be created across the pH range of interest, and phosphate does not absorb in the range of interest (250 – 350nm).

To demonstrate that the phosphate buffer did not influence the transformation process we compared the stability of O-MWCNTs buffered by acetate and phosphate at the same pH (4). Acetate was chosen because it is a widely used and commercially available buffer, we have used it in previous experiments to buffer at a pH of interest to this study, and it also it not compromised by the presence or absence of CO_2. Suspensions were prepared as described in the experimental section, buffered using either acetate or phosphate, and purged with nitrogen. The two suspensions were then placed into the Rayonet chamber and exposed to UVC light simultaneously, monitoring the absorbance and pH as a function of irradiation time, Figure S2 shows that the stability of the O-MWCNTs towards aggregation was the same in both buffers, demonstrating a lack of role of the phosphate buffer in the phototransformation process.

Calibration of Light Intensity via Actinometry

To determine the quantum flux produced by our UVC lamps we used a colorimetric actinometry experiment. As described in the experimental section of this paper, potassium

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ferrioxalate decomposes to form Fe^{2+} ions under irradiation, which then complexes with o-phenanthroline to form a red solution. The intensity of this red solution can be measured as a function of irradiation time to gauge the conversion rate of potassium ferrioxalate to Fe^{2+}, thereby enabling us to measure the intensity of light being emitted from our lamps.

Actinometry experiments were performed in the dark to eliminate light from the windows and overhead lights contributing to the decomposition of the ferrioxalate. Experimentally, 3mL of 0.006M ferrioxalate solution were put into the same 15mL quartz test tubes used to irradiate O-MWCNTs and exposed to irradiation for different prescribed periods of time (t). After each exposure period, 2mL of the irradiated solution was removed and mixed with 2mL of 0.0055M *o*-phenanthroline and 1mL of a pH 3.5 acetate solution to quench the reaction. This 5mL volume was then diluted to a 20mL total volume and stored for at least 1hr in the dark. This ensured that all of the Fe^{2+} produced by the UVC light had complexed with the *o*-phenanthroline. The optical density (D) of the solution was then measured at 510nm by UV-Vis to determine the concentration of the Fe^{2+}:*o*-phenanthroline complex and a plot of D *vs.* t was constructed. Until the supply of ferrioxalate has been consumed, D varies linearly with t, and in this regime Eq.1 can be used to determine the quantum flux (QF) using the expression:[4]

$$QF = \frac{DV_1V_3N10^{-3}}{t\Phi\varepsilon dV_2} \qquad \text{Eq. S1}$$

where V_1 is the volume of ferrioxalate solution irradiated (3mL), V_3 is the total end volume of solution (20mL), N is Avogadro's number, Φ is the quantum yield at the irradiation wavelength (for 254nm, Φ = 1.25), ε is the molar extinction coefficient of the ferrioxalate-phenanthroline complex at 510nm (1.11 x 10^4 L/mol·cm), d is the path length of the cuvette (1cm), and V_2 is the volume of irradiated solution used for complexation (2mL). Plots of D vs. t were constructed for different numbers of UVC lamps.

Part A of Figure S3 illustrates the plots of D vs. t for experiments performed with 16, 8, 6, 4, 2, and 0 lamps. A minimum of six time points were used for each different lamp number and fit using a linear regression to determine the average value of D/t needed to determine the QF in equation S1. Figure S3 shows that when the lamps are off, there is no residual light or photons being emitted from the lamps to induce any degradation of the ferrioxalate compound. As the number of lamps in the Rayonet chamber increases, that the light intensity as measured by D/t also increased linearly as a function of the number of lamps, except for experiments conducted with 16 lamps. Figure S3 shows us that there is no appreciable difference in the slope from 8 to 16 lamps. This effect is most likely due to the light intensity at both 8 and 16 lamps being sufficiently high so that not all of the photons are absorbed within the solution because all of the ferrioxalate has been consumed at the concentration used to measure the light intensity (0.006M, A_{254nm} = 3.6). Part B of Figure S3 shows the quantum flux calculated for each set of exposures using Eq. S1. A linear regression was used to determine the quantum flux for 16 lamps. (approximately 1.32 x 10^{17} quanta/sec).

For experiments performed with O-MWCNTs, the optical density of the O-MWCNT suspensions (5mg/L, A_{254nm} = 0.34) is an order of magnitude lower than that of the ferrioxalate. Consequently, the absorbance of the suspension in the quartz test tubes is expected to follow a

Beer-Lambert law regardless of the number of lamps used. Under these conditions the effective light intensity within each test tube will be directly proportional to the number of lamps.

Oxic versus Anoxic Conditions

Experiments were performed using nitrogen or oxygen as the purge gas to create anoxic and oxic conditions, respectively. The DO levels under these conditions was measured as a function of irradiation time using suspensions prepared with the same solution conditions and in the same way that O-MWCNT samples were prepared for UVC irradiation experiments. Initially, Figure S5 shows that there is a significant difference between the DO concentrations measured for samples prepared under oxic and anoxic conditions. However, as the irradiation time increases the DO levels become more comparable as the systems begin to equilibrate. However, even after 6hrs and equilibrium is reached where the DO level for a suspension prepared with an oxic purge (6.2mg/L) is roughly twice that for the one prepared using an anoxic purge (3.3mg/L).

References

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Figure S1

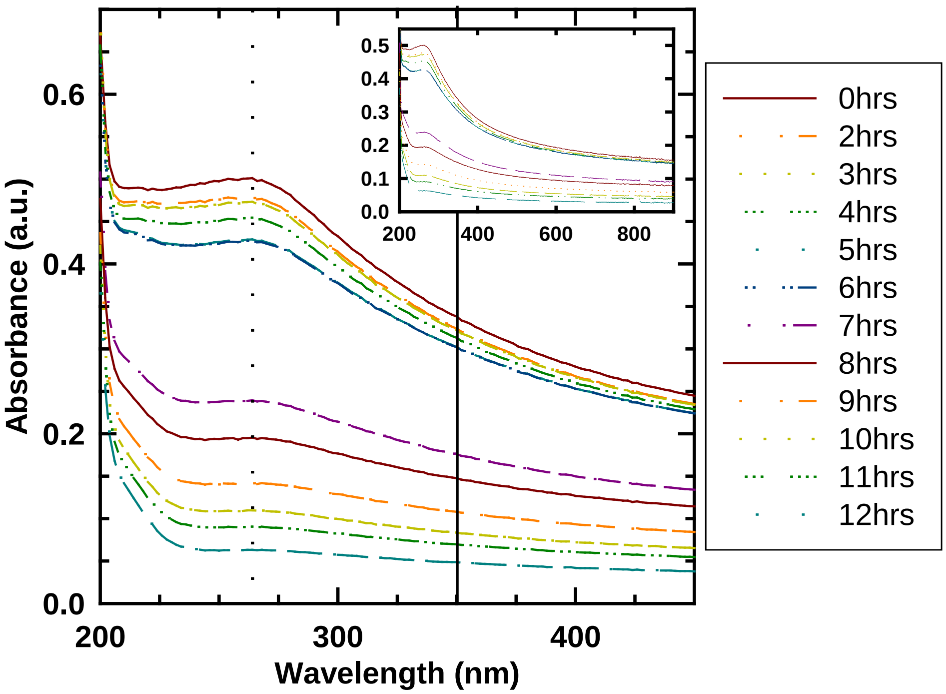

Figure S1 – UV-Vis absorbance spectra from 200 – 450nm of oxidized multiwalled CNTs at pH 7 and 12mM NaCl, purged with nitrogen and measured as a function of irradiation time. Absorption maximum (λ = 264nm) corresponds to the π → π* transition in the conjugated sidewall ring structure. The dashed line indicates the irradiation wavelength of 254nm, and the solid line indicates the wavelength at which measurements were taken (350nm). Inset shows the full spectra ranging from 200 – 900nm.

Figure S2

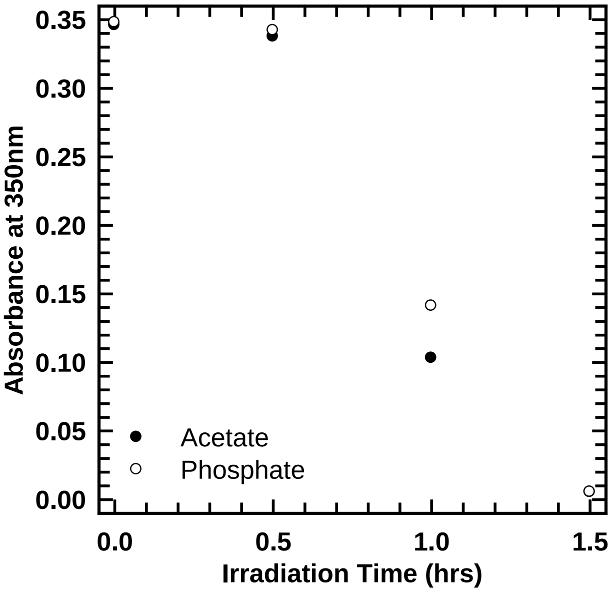

Figure S2 – Absorbance measurements for O-MWCNTs from NanoLab, Inc. under anoxic conditions using two common buffers to keep the suspension stable at pH 4.

Figure S3

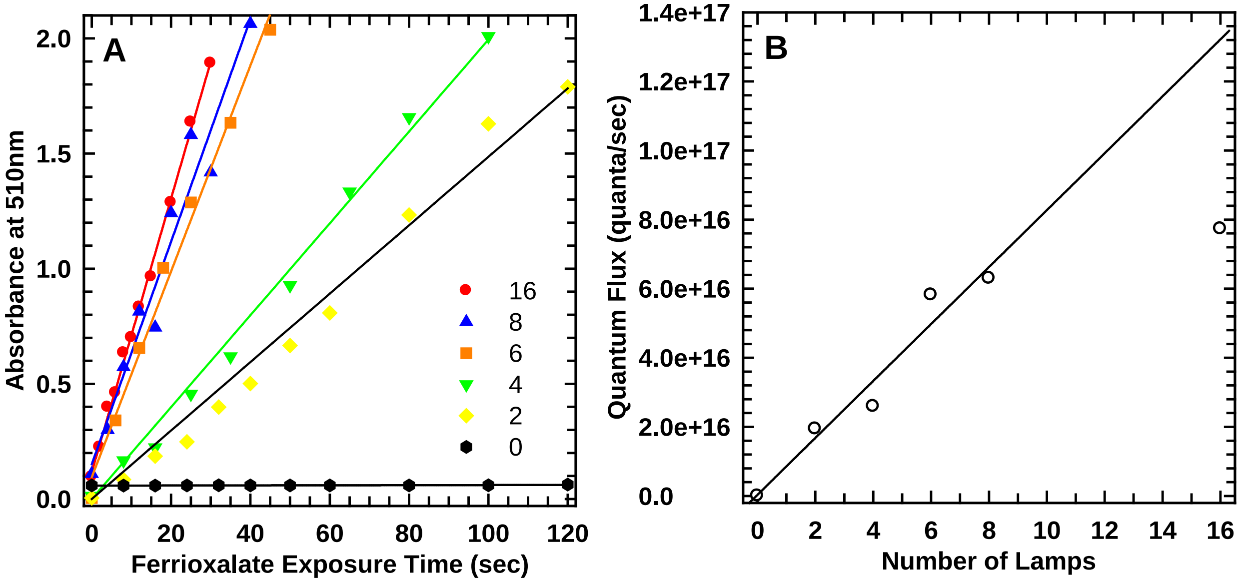

Figure S3 – Calibration curves (A) and the calculated quantum flux (B) for various lamp intensities measured with the ferrioxalate actinometry experiments.

Figure S4

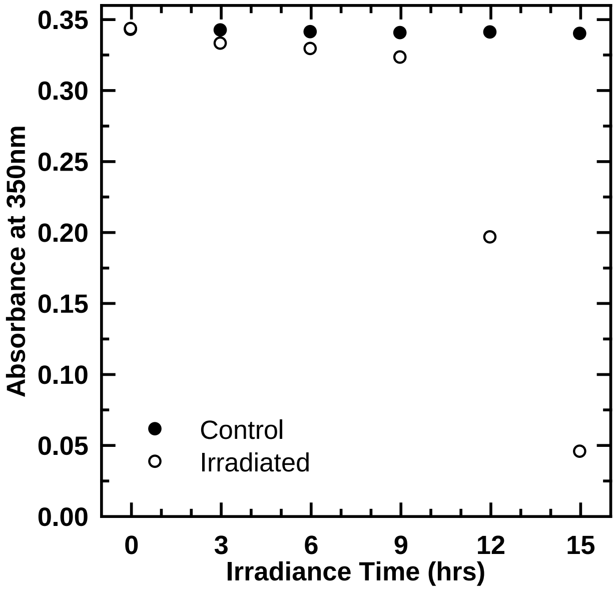

Figure S4 – Comparison of absorbance measurements for a control/dark sample and a sample exposed to UVC radiation at pH 7 and 3mM Na^+.

Figure S5

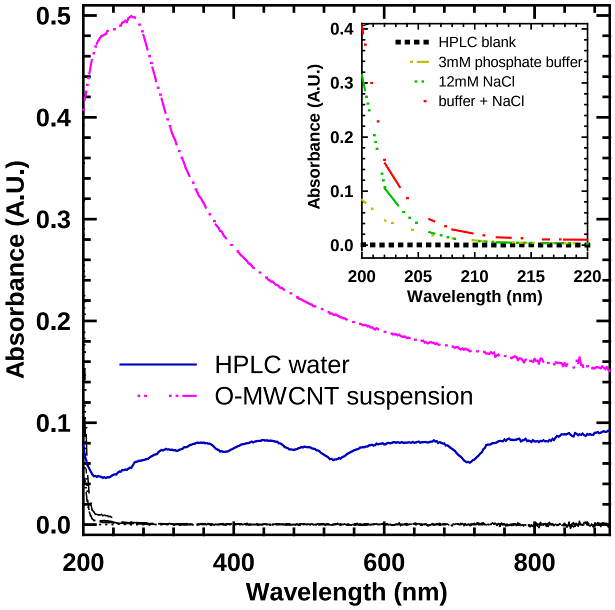

Figure S5 – UV-Vis absorbance spectra from 200 – 900nm for the individual constituents that make up an O-MWCNT suspension. The inset shows the region from 200 – 220nm to show the increase displayed in the absorbance profiles of the 3mM phosphate buffered water and the 12mM NaCl solution. These contributions can be seen in the profiles of the experimental O-MWCNT suspension from Figure S1.

Figure S6

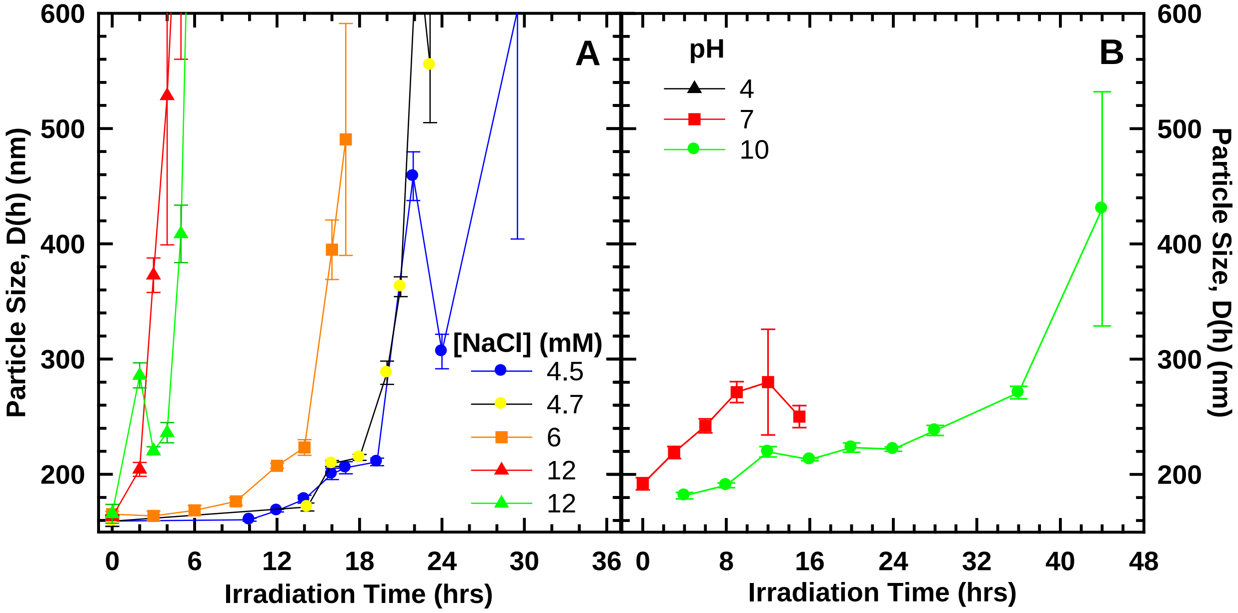

Figure S6 – Particle size measurement profiles for oxidized multiwalled CNTs under anoxic conditions as a function of ionic strength (A) and pH (B) plotted as a function of UV irradiation time.

Figure S7

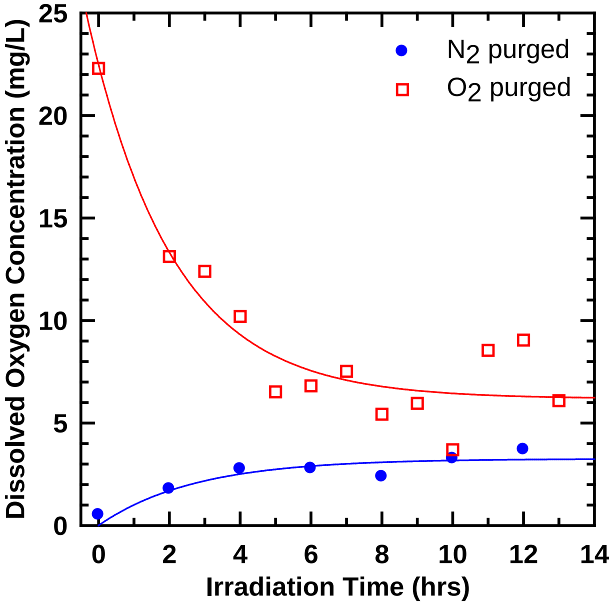

Figure S7 – The change in total dissolved oxygen plotted as a function of irradiation time measured from the same experiment as shown in Figure 6.

Table S1

Table S1 – Calculation of the quantum flux for 16, 8, 6, 4, 2, and 0 lamps. Flux is determined by actinometric measurements performed with potassium ferrioxalate. The quantum flux listed for 16 lamps appears twice to indicate that which was actually measured during the actinometry experiment, and what the likely flux is based on extrapolation via linear regression of the data from 0 – 8 lamps.

Number of Lamps	Quantum Flux (quanta/sec)
0	3.07×10^{11}
2	1.94×10^{16}
4	2.59×10^{16}
6	5.82×10^{16}
8	6.30×10^{16}
16 (measured)	7.73×10^{16}
16 (extrapolated)	1.32×10^{17}

Table S2

Table S2 – XPS measurements performed on various O-MWCNTs before and after irradiation with 254nm UVC light for various O-MWCNTs under oxic or anoxic conditions at pH 10. Only the total oxygen percent is shown, the percent carbon is neglected, but the %C + %O = 100%. For example, if the %O = 7.5%, the carbon peak result was 92.5%. The numbers in parentheses show the percentage of carboxylic acid groups that were measured before and after irradiation. The asterisk (*) indicates that the experiment was performed at pH 7 instead of pH 10.

Manufacturer	Gas Purge	%Oxygen Before Irradiation	%Oxygen After UV-Induced Aggregation
NanoLabs, Inc.	Nitrogen	7.5 (1.7)	5.1 (0.6)
NanoLabs, Inc.	Oxygen	7.5 (1.7)	6.1 (1.3)
Cheaptubes	Nitrogen	9.0 (0.7)	7.2 (0.5)
Cheaptubes	Oxygen	9.0 (0.7)	5.1 (0.4)
NanoLabs, Inc.	Nitrogen	9.0 (3.2)	5.9 (2.2)
Cheaptubes	Oxygen	6.9 (0.9)	6.8 (0.3)
NanoLabs, Inc.	Nitrogen	9.5 (1.7)	6.5 (0.8)
NanoLabs, Inc.*	Nitrogen	7.9 (1.8)	6.3 (0.4)