Supporting Information

Phototransformation-Induced Aggregation of Functionalized Single-Walled Carbon Nanotubes: the Importance of Amorphous Carbon

Wen-Che Hou,†, Chen-Jing He†, Yi-Sheng Wang†, David K. Wang⊥, Richard G. Zepp*,§*

† Department of Environmental Engineering, National Cheng Kung University, Tainan City, Taiwan 70101

§National Exposure Research Laboratory, Exposure Methods & Measurement Division, U. S. Environmental Protection Agency, Athens, GA, 30605

⊥The University of Queensland, FIMLab - Films and Inorganic Membrane Laboratory, School of Chemical Engineering, Brisbane Qld 4072, Australia.

**Address correspondence to either author. Phone: +886 62757575 ext.65842 (W. C. H.). (706) 355-8117, E-mail: whou@mail.ncku.edu.tw (W. C. H.); Zepp.Richard@epa.gov (R. G. Z.).*

Manuscript prepared for publication in: Environmental Science & Technology

Pages: 12

Figures: S1-7

Table: S1-2

Procedure to establish calibration curve for concentrations of carboxylated SWCNT

Immediately following dispersion of carboxylated SWCNT (10 mg in 100 mL water), the stock dispersion was serially diluted with pure water to lower concentrations whose light absorbances were recorded. The calibration curve was constructed by plotting the absorbances versus mass concentrations. The calibration curve is presented in Figure S1.

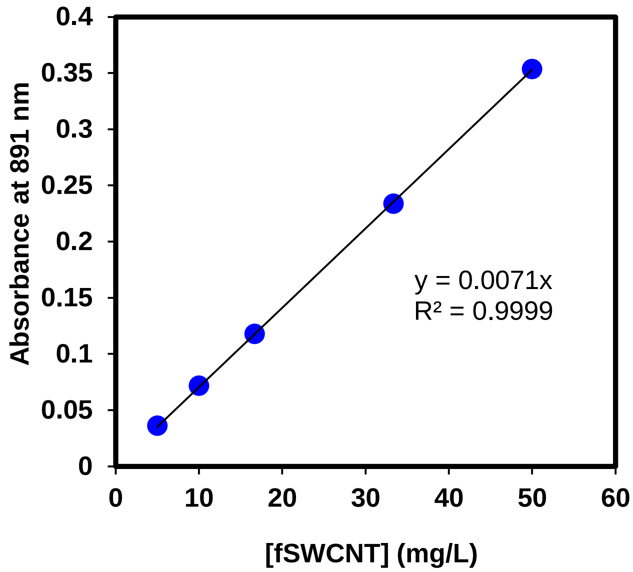

Figure S1. Calibration curve of carboxylated SWCNTs.

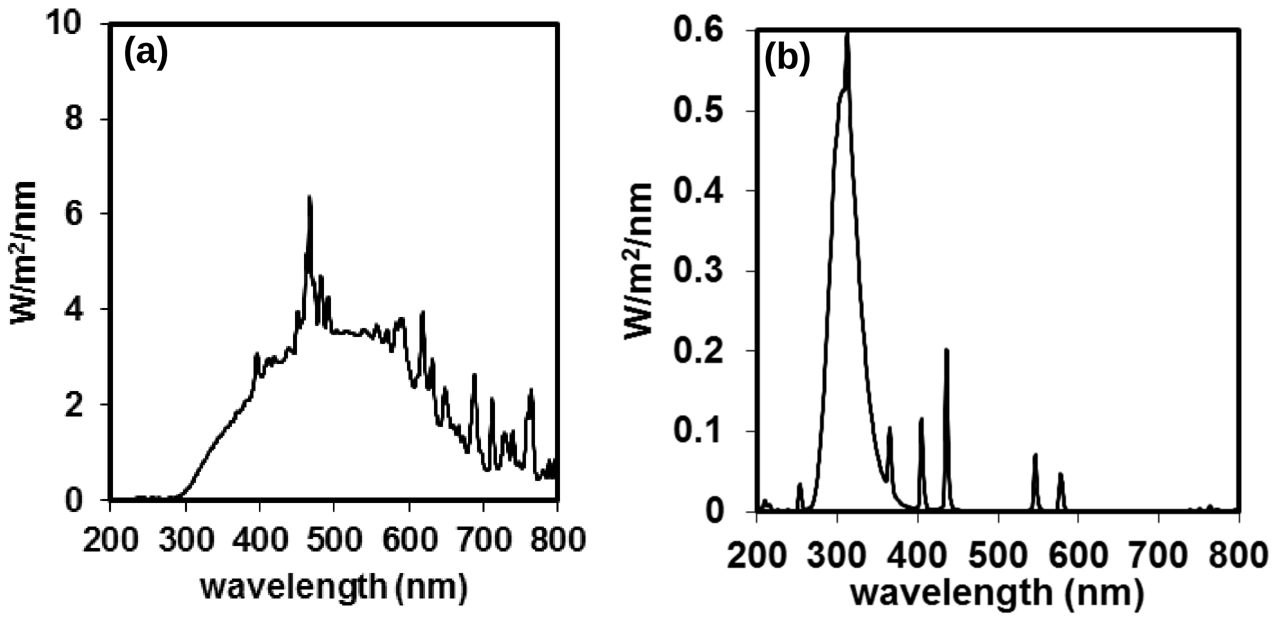

Figure S2. Light emission spectrum of (a) the solar simulator and (b) 315-nm lamps (4 lamps).

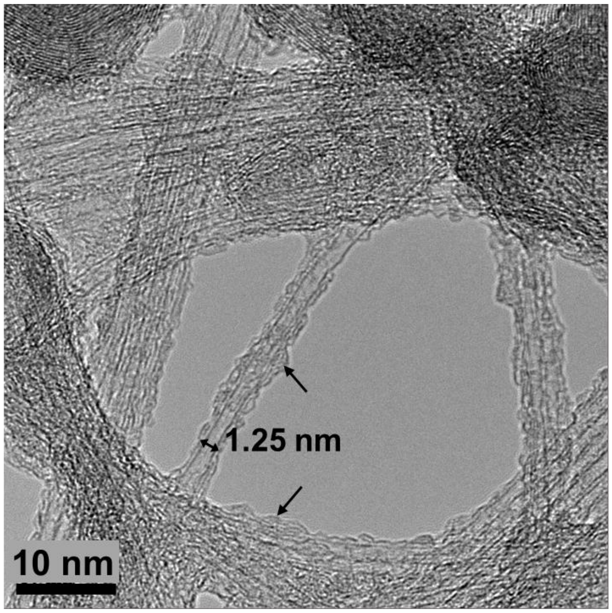

Figure S3. TEM images of parent carboxylated SWCNT. Arrows highlight the presence of amorphous carbon.

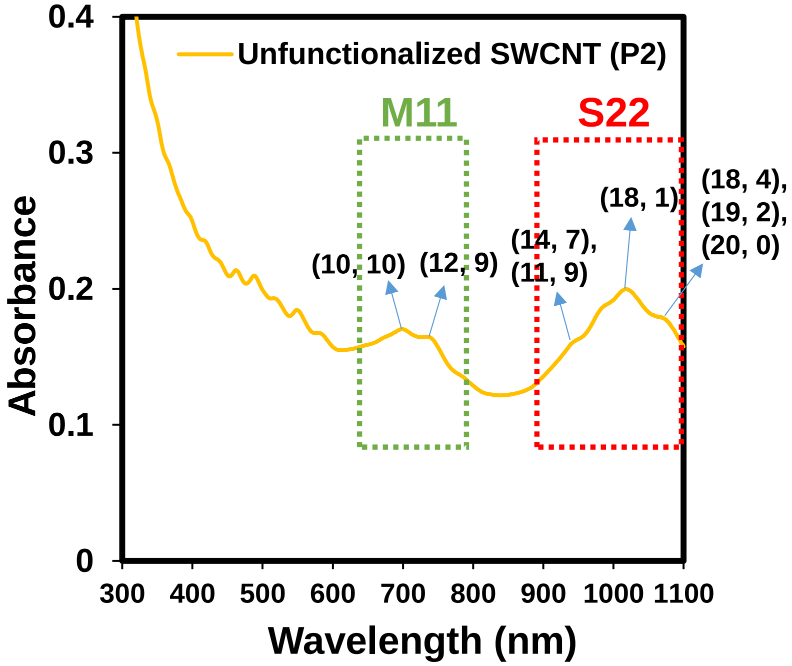

Figure S4. UV-visible-NIR absorbance spectrum of unfunctionalized SWCNT (P2) dispersed in 1% (w/w) sodium deoxycholate. The spectrum of pristine non-functionalized P2 SWCNT is presented, as the electronic transitions can be quenched as result of SWCNT oxidation (e.g., carboxylation) as in P3 sample.[1] The P2 sample is the precursor used to manufacture of carboxylated SWCNT (P3 sample).

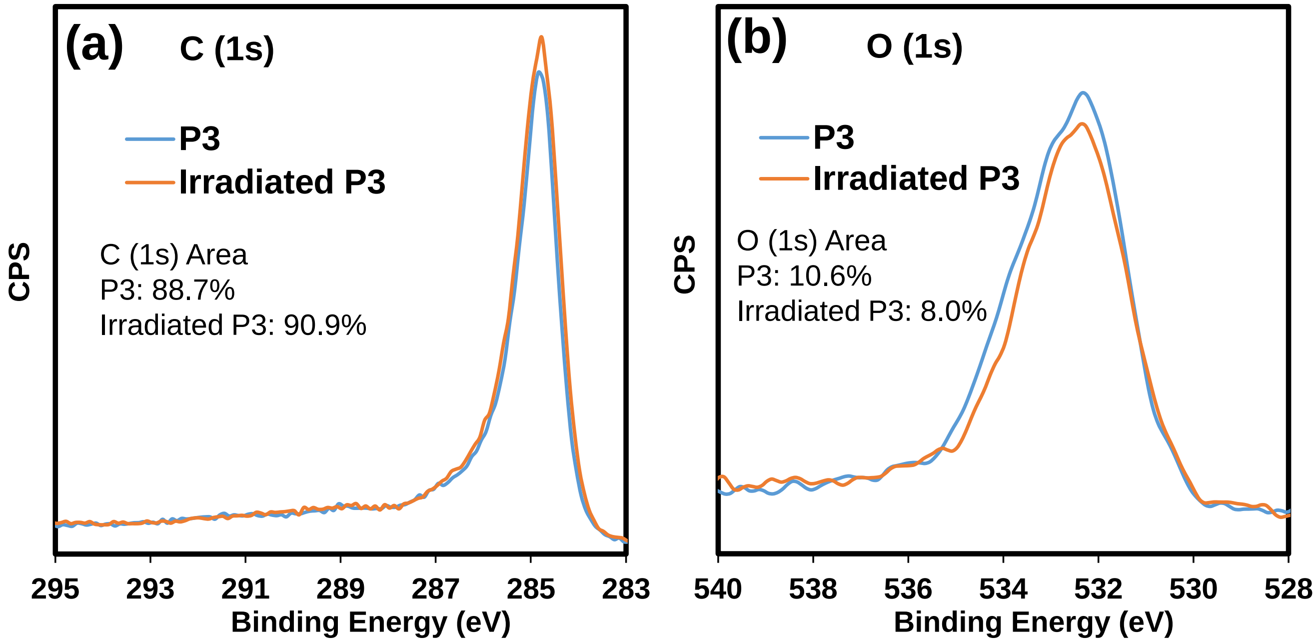

Figure S5. XPS spectra of carboxylated SWCNT before and after 300 h of simulated sunlight irradiation in the presence of H_2O_2, showing spectral envelopes of the (a) C (1s) and (b) O (1s) regions and corresponding areas.

Table S1. Elemental analysis of SWCNT samples by EDS.

Element	P3	P33
C	91.82 ± 1.20	94.93 ± 0.19
O	7.18 ± 1.12	4.36 ± 0.07
Ni	1.00 ± 0.08	0.71 ± 0.16

Errors indicate one standard deviation.

The EDS data shown in Table S1 indicate that the metal catalyst impurity is a minor component of the SWCNT samples (<1 atomic %) compared to carbon and oxygen. While metal catalyst impurity has been shown to mediate OH radical formation in carbon nanotube samples,[2,3] the smaller residual Ni catalyst content in the P33 sample does not correlate with its reduced stability under indirect photolysis conditions (Figure 4) as ·OH reaction would decrease SWCNT stability.

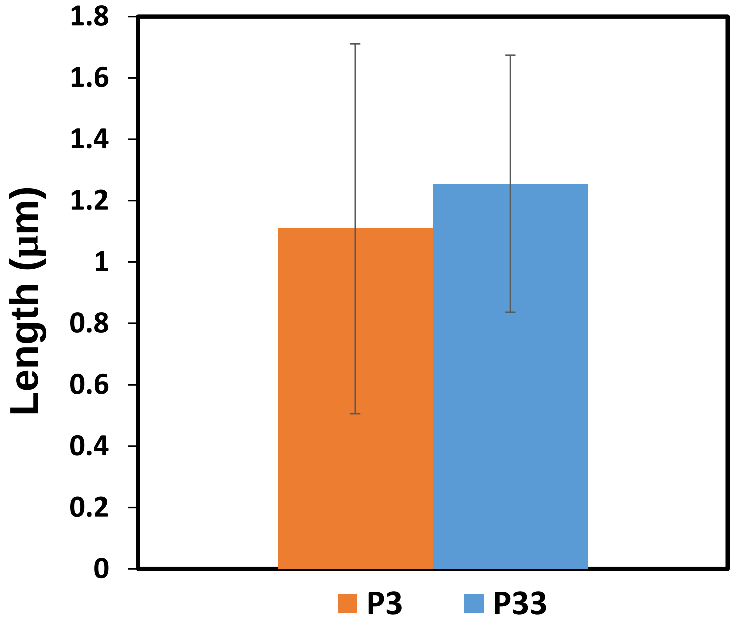

Figure S6. Lengths of P3 and P33 samples analyzed with AFM. The error bars indicate ± one standard deviation. The results are from analysis of three separate AFM samples. The representative AFM images are presented in Figure S7.

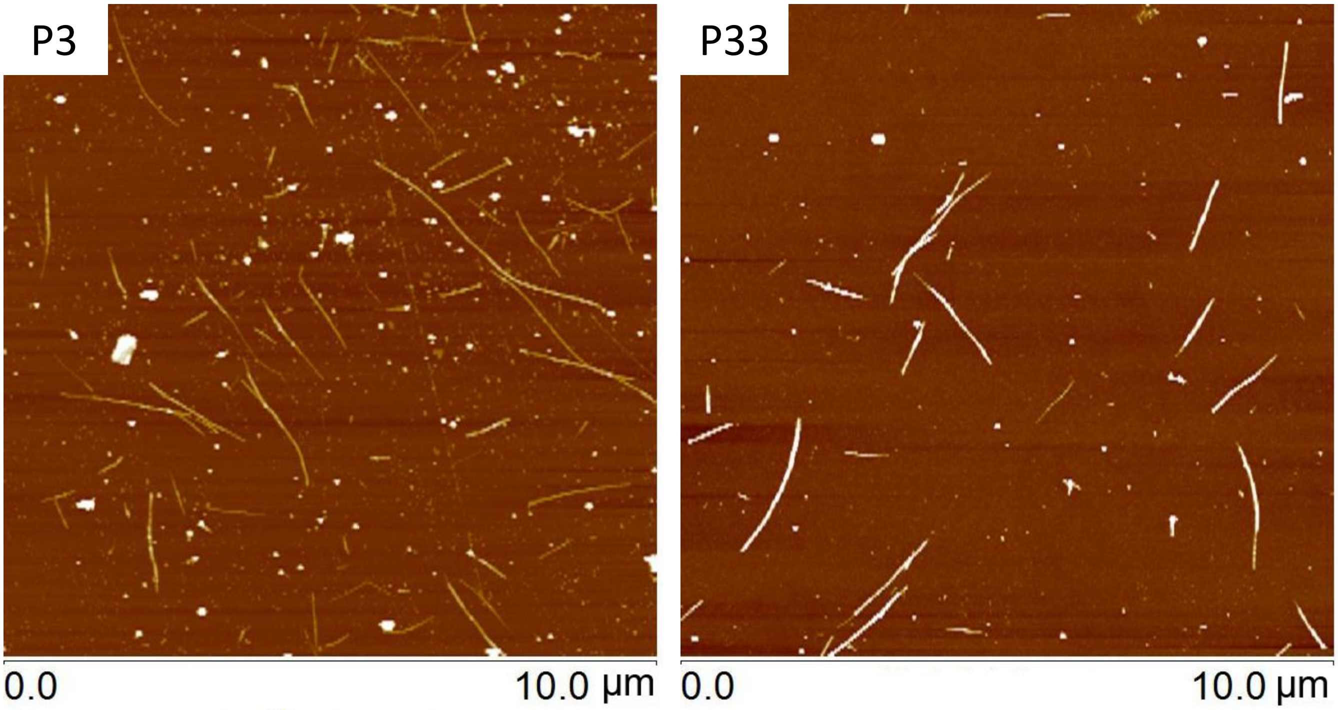

Figure S7. Representative AFM images of P3 and P33 samples.

Table S2. Summary of parameters derived from the kinetic study presented in Figure 5.

Sample	$[\cdot OH]_{ss}$ (M)	SF[a]	[b]$[\cdot OH]_{ss,corrected}$ (M)	$k_{\cdot OH,H2O2}[H_2O_2]$ (s^{-1})	$k_{\cdot OH,pCBA}$[pCBA] (s^{-1})	$k_{\cdot OH,octanol}$[octanol] (s^{-1})	$k_{\cdot OH,SWCNT}$[SWCNT] (s^{-1})	$k_{\cdot OH,SWCNT}$ ($M_{as\ C}^{-1}s^{-1}$)
H_2O_2 only	$(4.5 \pm 0.15) \times 10^{-13}$	NA	4.5×10^{-13}	6.8×10^{4}	1.3×10^{4}	NA	NA	NA
1.26 mM octanol	$(5.2 \pm 0.14) \times 10^{-14}$	NA	5.2×10^{-14}	6.8×10^{4}	1.3×10^{4}	7.6×10^{6}	NA	NA
5 mg/L P3	$(2.5 \pm 0.34) \times 10^{-13}$	0.83	3.0×10^{-13}	6.8×10^{4}	1.3×10^{4}	NA	1.3×10^{6}	3.1×10^{9}
10 mg/L P3	$(1.9 \pm 0.42) \times 10^{-13}$	0.68	2.8×10^{-13}	6.8×10^{4}	1.3×10^{4}	NA	1.4×10^{6}	1.7×10^{9}
5 mg/L P33	$(2.4 \pm 0.22) \times 10^{-13}$	0.77	3.1×10^{-13}	6.8×10^{4}	1.3×10^{4}	NA	1.6×10^{6}	3.8×10^{9}
10 mg/L P33	$(1.9 \pm 0.31) \times 10^{-13}$	0.58	3.2×10^{-13}	6.8×10^{4}	1.3×10^{4}	NA	1.6×10^{6}	1.9×10^{9}

NA: not applicable

[a]SF: light screening factor

[b]$[\cdot OH]_{ss,corrected} = [\cdot OH]_{ss} / SF$.

Reference

(1) Hou, W.-C.; BeigzadehMilani, S.; Jafvert, C. T.; Zepp, R. G. Photoreactivity of Unfunctionalized Single-Wall Carbon Nanotubes Involving Hydroxyl Radical: Chiral Dependency and Surface Coating Effect. *Environ. Sci. Technol.* **2014**, *48* (7), 3875–3882.

(2) Chen, C.-Y.; Jafvert, C. T. Photoreactivity of Carboxylated Single-Walled Carbon Nanotubes in Sunlight: Reactive Oxygen Species Production in Water. *Environ. Sci. Technol.* **2010**, *44* (17), 6674–6679.

(3) Chen, C.-Y.; Jafvert, C. T. The role of surface functionalization in the solar light-induced production of reactive oxygen species by single-walled carbon nanotubes in water. *Carbon* **2011**, *49* (15), 5099–5106.