

Photochemical Fate of Carbon Nanotubes in the Aquatic Environment

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Students Supported

Graduated

- Julie Bitter, Dissertation Title: “Fate and Tracking of Engineered Nanomaterials in Aqueous Environments”, Johns Hopkins University, March 2014. (Currently an NRC post-doctoral fellow at NIST)

In Progress

- Timothy Berry, Dissertation Title: Microbial Controls on the Environmental Fate of Carbon Nanomaterials, Purdue University, anticipated graduation in December 2015
- Somayeh BeigzadahMilani, Dissertation Title: Photochemistry and Extraction of Carbon Nanotubes in the Natural Environment”, Purdue University, anticipated graduation in May, 2015

Partially Supported

- Chia-Ying Chen, Dissertation Title: “Sorption and Photochemistry of Manufactured carbon Nanomaterials in the Aquatic Environment”, Purdue University, December, 2010.

In Progress, Partially Supported:

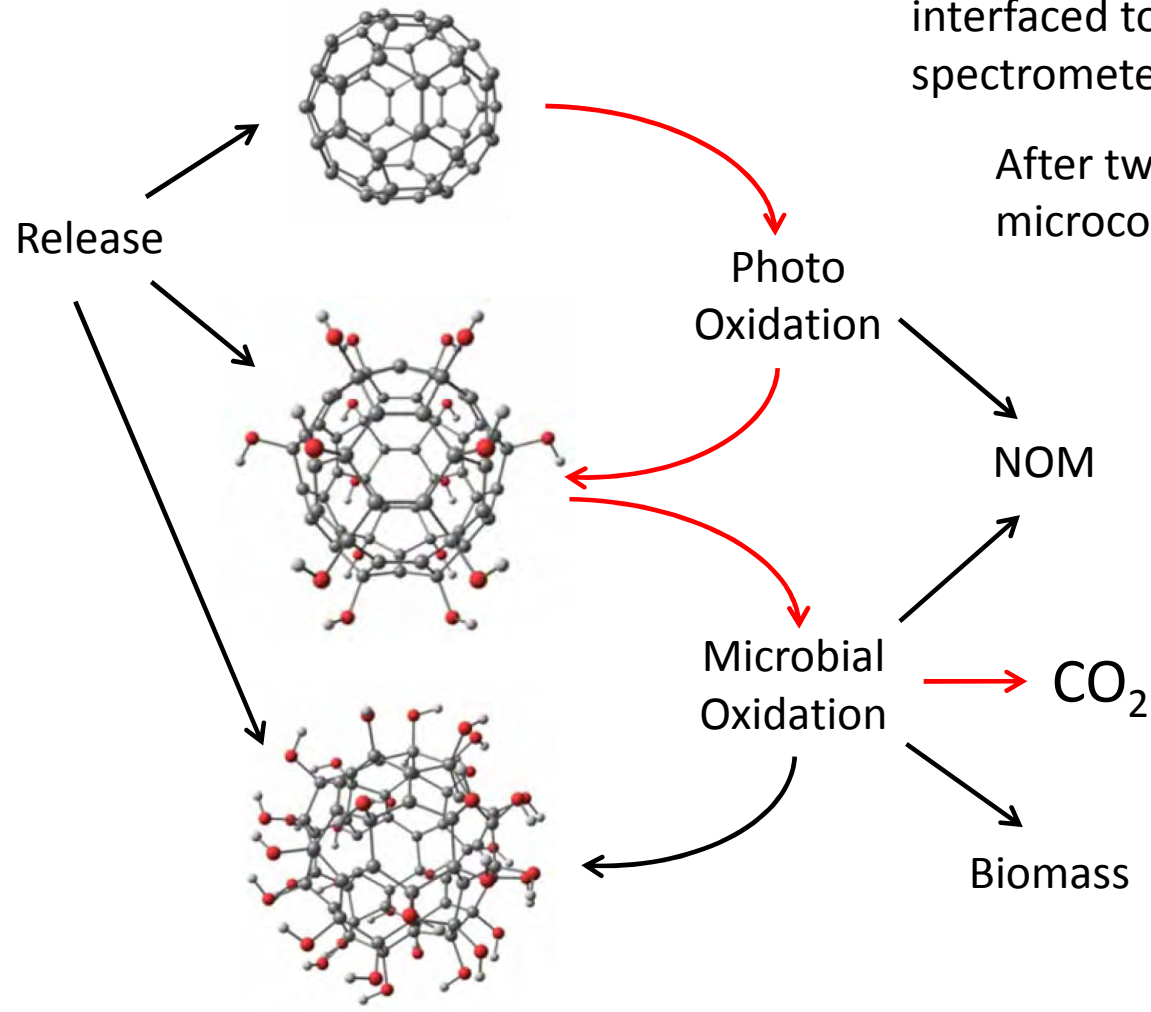
- Hsin-Se Hsieh, Dissertation Title: “Carbon nanotubes mediated redox reactions in water: reactive oxygen species generation and pollutant reduction”, anticipated graduation in May 2015
- Yingcan Zhou, Dissertation Title: “Environmental Reactions of Graphene Oxide”, Purdue University, anticipated graduation in December 2015

Published Papers (to date)

- Chen, Chia-Ying; Jafvert, Chad T., “The Role of Surface Functionalization in the Solar Light-Induced Production of Reactive Oxygen Species by Single-Walled Carbon Nanotubes in Water”, *Carbon*, 49:5099-5106, 2011.
- Berry, Timothy D.; Filley, Timothy R.; Blanchette, Robert A., “Oxidative Enzymatic Response of White-Rot Fungi to Single-Walled Carbon Nanotubes”, *Environmental Pollution*, 193:197-204, 2014.
- Hou, Wen-Che, Somayeh BeigzadahMilani, Chad T. Jafvert, Richard G. Zepp, “Photoreactivity of Unfunctionalized Single-Walled Carbon Nanotubes Involving Hydroxyl Radical: Chiral Dependency and Surface Coating Effects”, *Environ. Sci. Technol.*, 48: 3875-3882, 2014.
- Bitter, Julie L., Jin Yang, Somayeh BeigzadehMilani, Chad T. Jafvert, d. Howard Fairbrother, Transformations of Oxidized Multiwalled Carbon Nanotubes exposed to UVC (254 nm) irradiation, *Environmental Sciences: Nano*, 1, 324-337, 2014.
- Hsieh, Hsin-Se, Renren Wu, Chad T. Jafvert, “Light-Independent Reactive Oxygen Species (ROS) Formation through Electron Transfer from Carboxylated Single-Walled Carbon Nanotubes in Water”, in press, *Environ. Sci. Technol.*, 2014.

Coupled Processes

- Aqueous suspensions of ^{13}C -enriched C_{60} were progressively oxidized by artificial sunlight.
- CO_2 volume and isotopic composition was determined with a trace-gas analyzer interfaced to an isotope ratio mass spectrometer

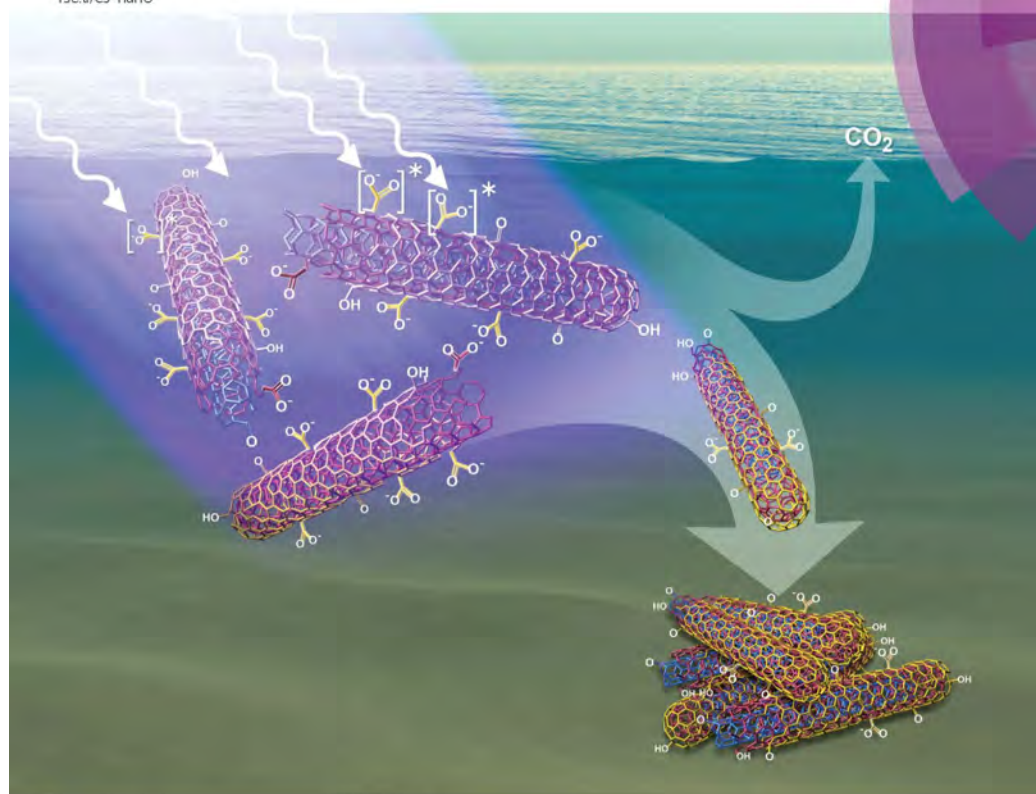


After two months of incubation in soil microcosms (2 mg nanocarbon / 3 g soil)

- C_{60} photo-treated for 60 days produced significant ^{13}C -enriched CO_2 .
- C_{60} photo-treated for 0 or 10 days produced no ^{13}C -enriched CO_2 .

Environmental Science Nano

rsc.li/es-nano

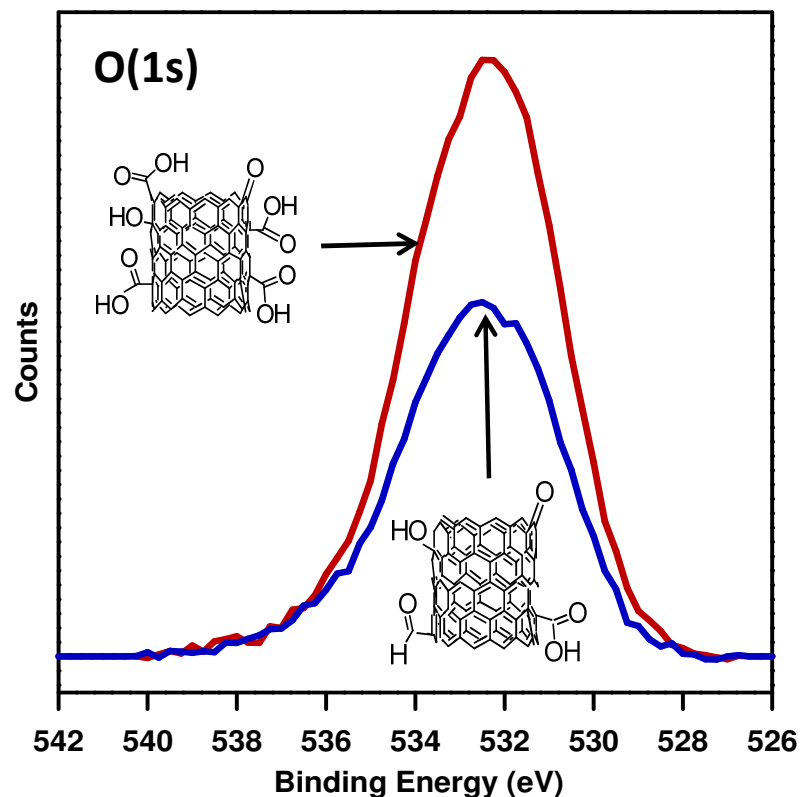


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PAPER
D. Howard Fairbrother et al.
Transformations of oxidized multiwalled carbon nanotubes exposed to UVC (254 nm) irradiation

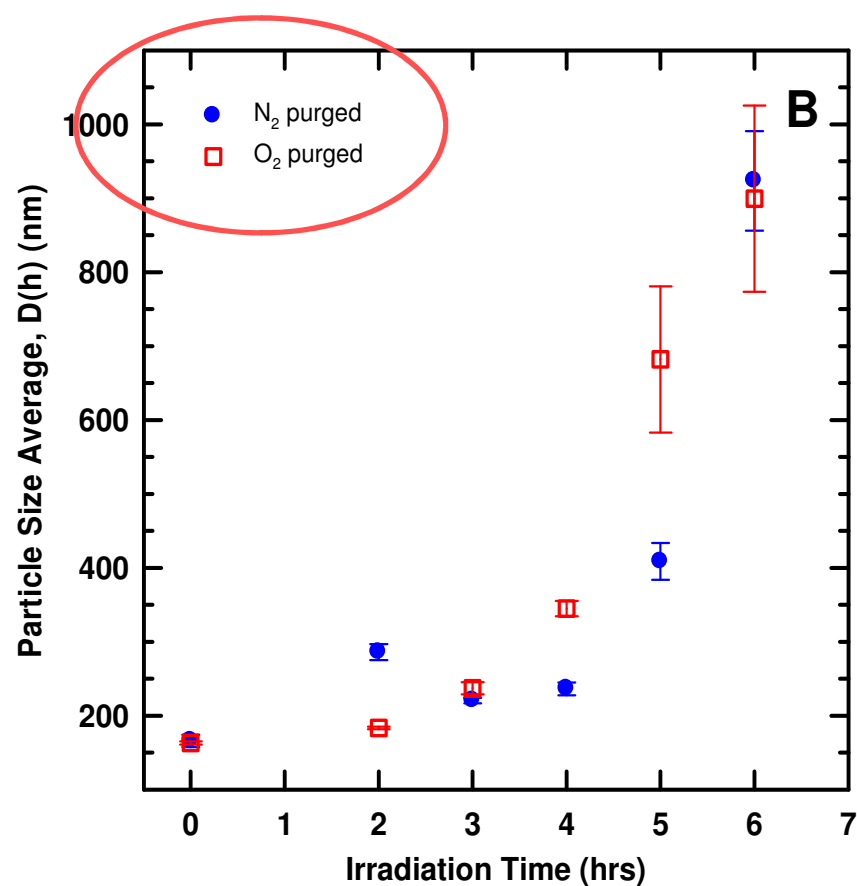
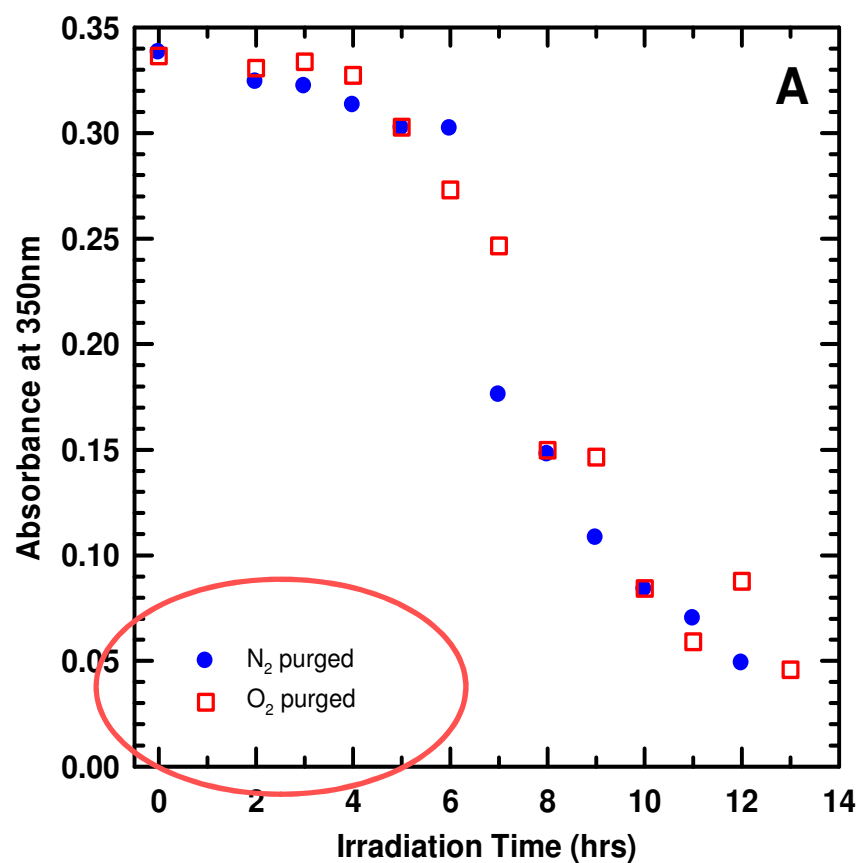
XPS Analysis shows that aggregation is driven by a loss of oxygen from the CNT surface



Bitter, Julie L., Jin Yang, Somayeh BeigzadehMilani, Chad T. Jafvert, d. Howard Fairbrother, Transformations of Oxidized Multiwalled Carbon Nanotubes exposed to UVC (254 nm) irradiation, *Environmental Sciences: Nano*, 1, 324-337, 2014.

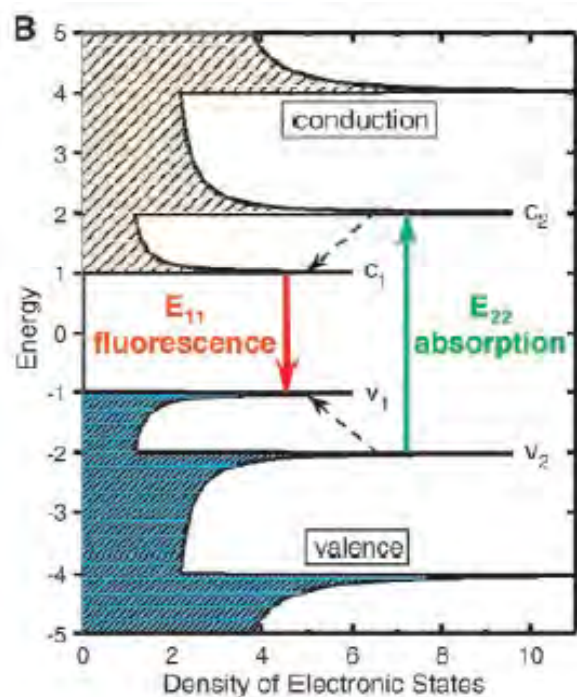
Dissolved oxygen does not affect the kinetics

Suggests Direct Decarboxylation

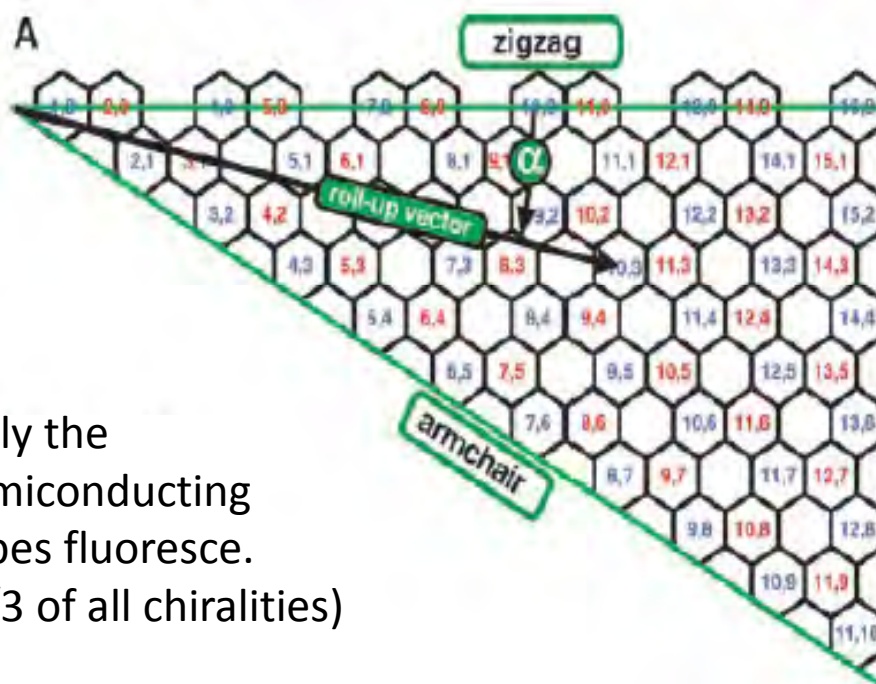


Indirect Photo-Oxidation of Unfunctionalized Carbon Nanotubes

Light absorption at photon energy E_{22} followed by fluorescence emission at E_{11}



Nanotubes designated (n,m) obtained by rolling sheet from (0,0) to (n,m) along with chiral vector

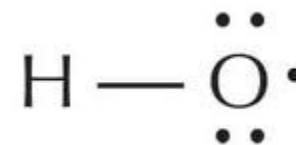


Only the semiconducting tubes fluoresce.
(2/3 of all chiralities)

Image from Bachilo et al., 2002

Hou, Wen-Che, Somayeh BeigzadahMilani, Chad T. Jafvert, Richard G. Zepp, "Photoreactivity of Unfunctionalized Single-Walled Carbon Nanotubes Involving Hydroxyl Radical: Chiral Dependency and Surface Coating Effects", *Environ. Sci. Technol.*, 48: 3875-3882, 2014.

Hydroxyl Radicals



- Second-order rate constants for reaction with organic compounds are in the range of 10^7 – $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ (Buxton et al., 1988).
- Plays a significant role in the phototransformation of organic compounds in natural waters.

| Water body | NO_3^- (mg of N/L) | DOC (mg/L) | $[\cdot\text{OH}]_{\text{ss}}$ (M) |
|---|--------------------------------|---------------|---------------------------------------|
| Small lake such as Geifensee ^a | 1.4 | 4 | 2.5×10^{-16} |
| Shallow water body, rich in NO_3^- , such as water with large groundwater input ^a | 14 | 2 | 5×10^{-15} |
| Blue Earth River ^b | 8.8 | 4.19 | 9.9×10^{-16} |
| Lake Minnetonka ^b | 0.27 | 7.45 | 3.1×10^{-17} |
| Lake Nichols ^b | 0.13 | 6.23 | 2.5×10^{-17} |

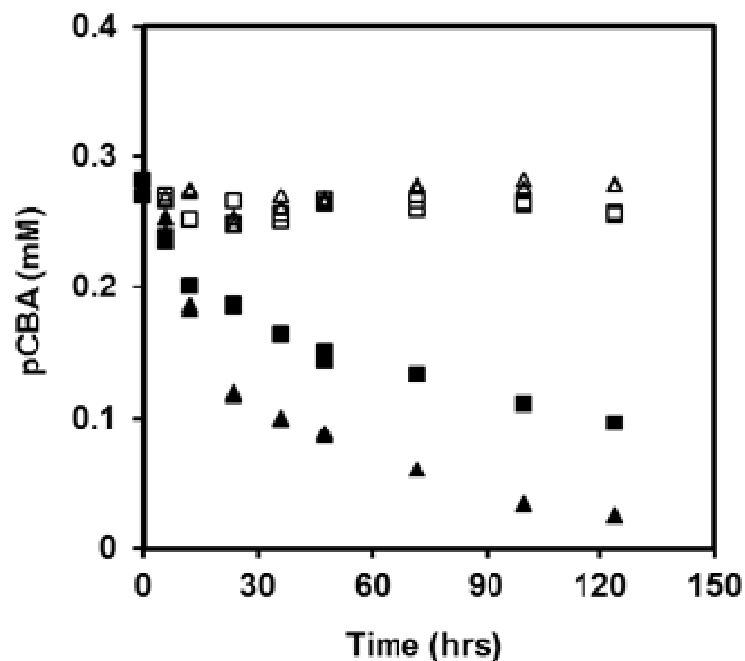
Data from:

^a Zepp et al. (1987)

^b Patrick et al. (1998)



Hydroxyl Radical Steady-State Concentration (w/ SDS)



Irradiated pristine SG-65 in 0.5% SDS ,100 mM H₂O₂ (■)

Dark control of pristine sg-65 in 0.5 % SDS, 100 mM H₂O₂ (□)

Irradiated 0.5% SDS, 100 mM H₂O₂ (▲)

Dark control of 0.5 % SDS, 100 mM H₂O₂ (△)

$$-\frac{d[pCBA]}{dt} = k_{OH,pCBA}[\cdot OH]_{ss} [pCBA]$$

$$-\frac{d[pCBA]}{dt} = k_{exp} [pCBA]$$

$$[\cdot OH]_{ss} = \frac{k_{exp}}{k_{OH,pCBA}}$$

| Sample information | Irradiation period (hrs) | [$\cdot OH$] _{ss} (M) |
|--------------------------|--------------------------|--|
| SG-65 in 0.5% SDS | 124 | 4.17×10^{-16} |
| 0.5 % SDS | 124 | 1.01×10^{-15} |

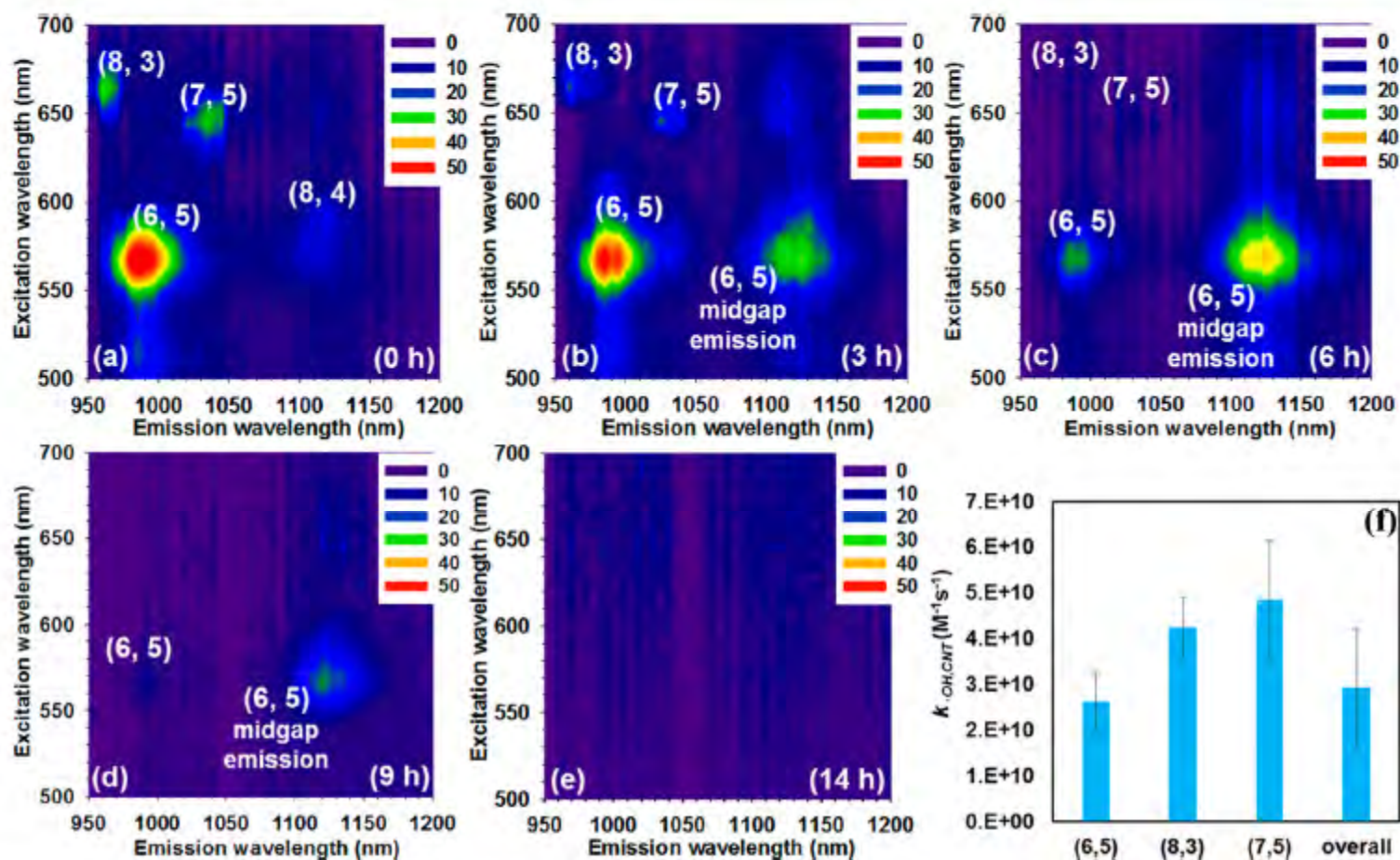
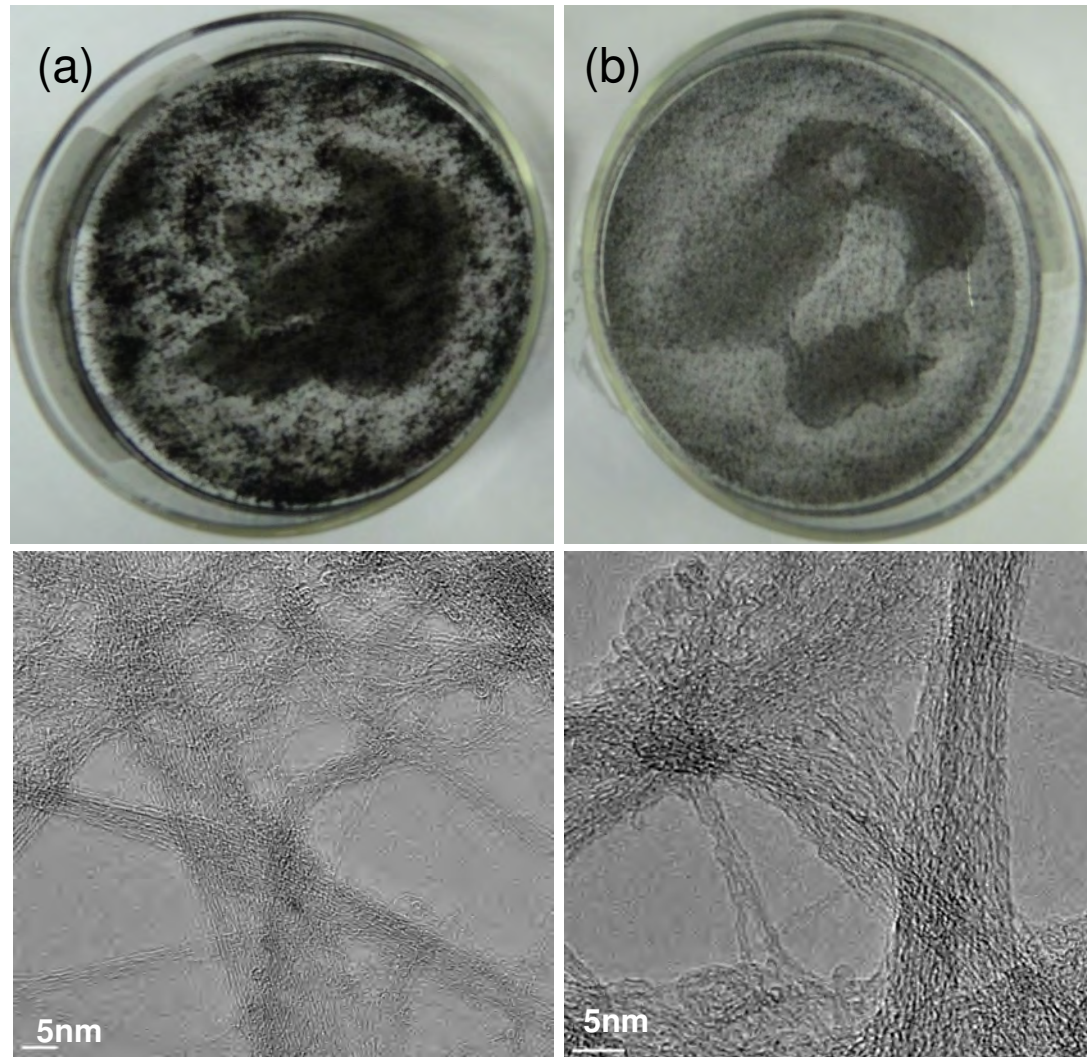


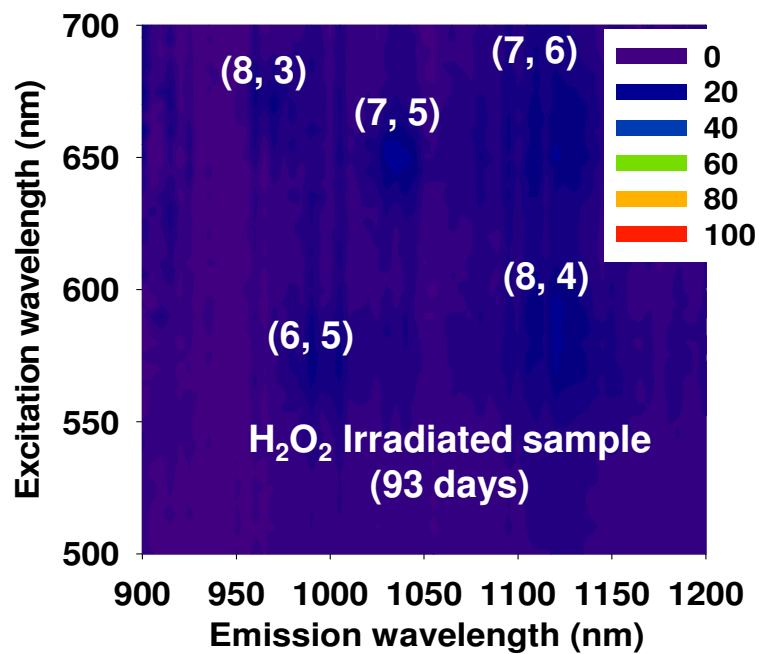
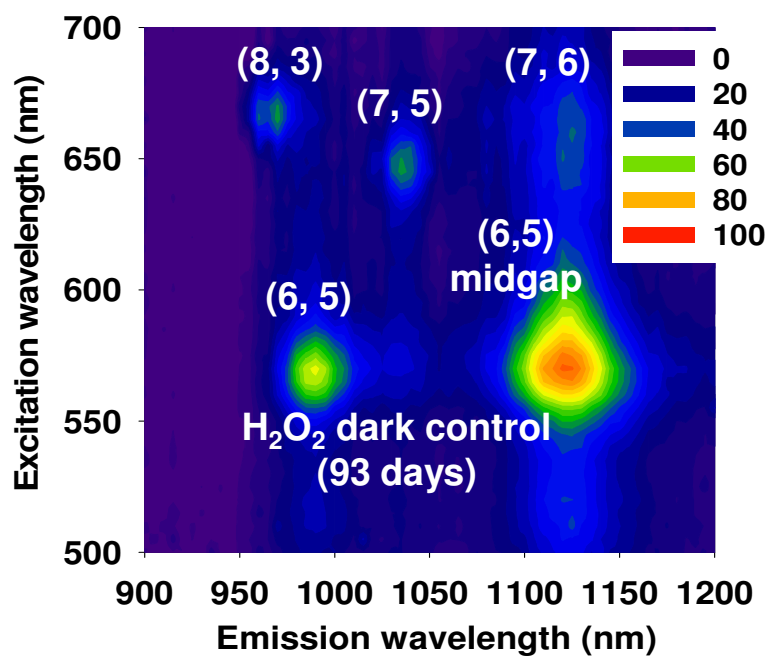
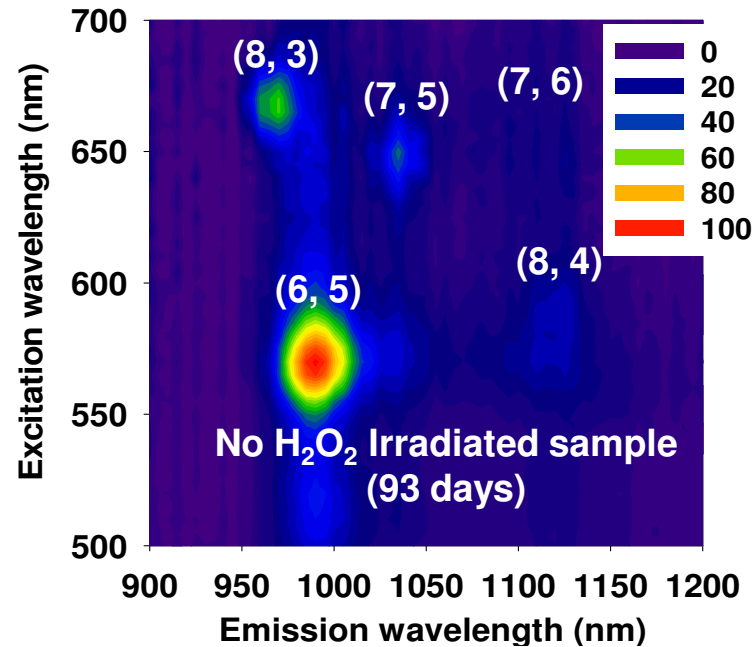
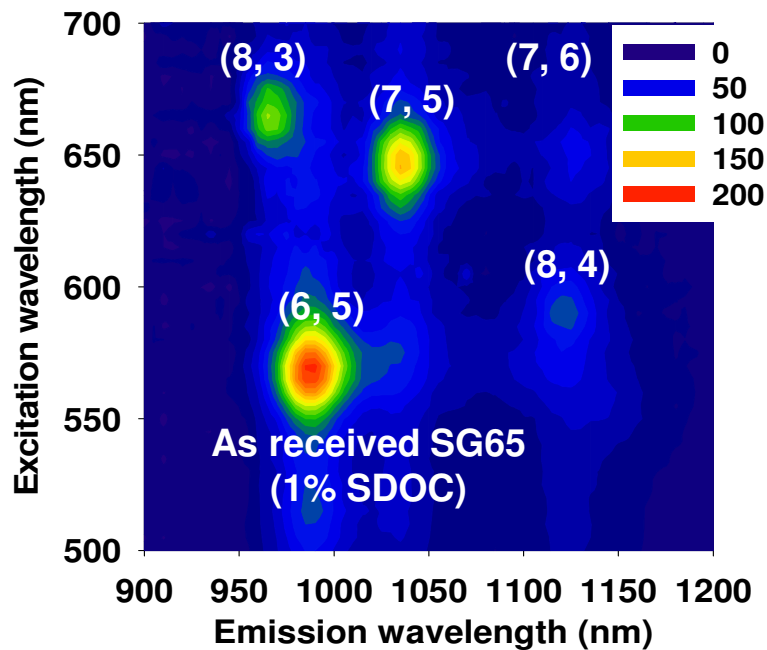
Figure 3. Time-resolved EEM showing (a–e) the fluorescence quenching of SG65 SWCNT in the presence of 100 mM H_2O_2 under sunlight exposure at pH = 7.0. Panel f indicates the operationally defined second-order rate constants for $\cdot\text{OH}$ reaction with different chiral components and with SWCNTs as a whole. The SG65 SWCNT sample was dispersed in 1% SDS. The error bars indicate 95% confidence intervals.

Surfactant-free unfunctionalized SG65 w/ hydrogen peroxide



- a) 68 days, dark control
- b) 68 days, with light irradiation

Bleaching after 93 days irradiation with hydrogen peroxide



XPS shows changes in oxygen content of photo-irradiated tubes with hydrogen peroxide

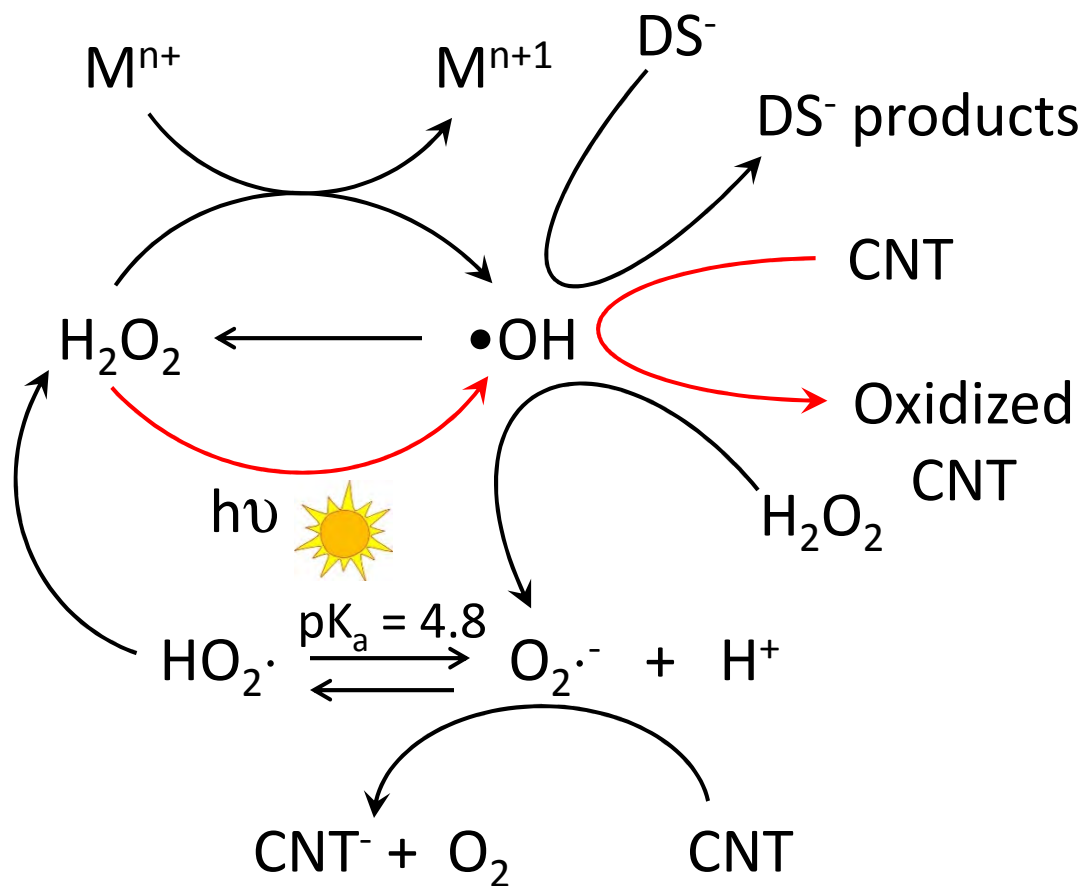
| Sample ID | Total % O | %O(C-OH) | %O(COOH) | %O (C=O) | O(other) |
|--|-----------|----------|----------|----------|----------|
| as-received SG65 | 4.4 | 0.7 | 1.4 | 2.5 | -0.2 |
| dark control SG65 w/ H ₂ O ₂ | 11.7 | 1.9 | 0.8 | 3.4 | 5.6 |
| irradiated SG65 w/o H ₂ O ₂ | 11.0 | 2.1 | 1.9 | 3.0 | 4.0 |
| irradiated SG65 w/ H ₂ O ₂ | 16.5 | 2.6 | 0.8 | 3.3 | 9.8 |

Oxygen-containing functional groups such as ethers, esters, and epoxides show highest increase

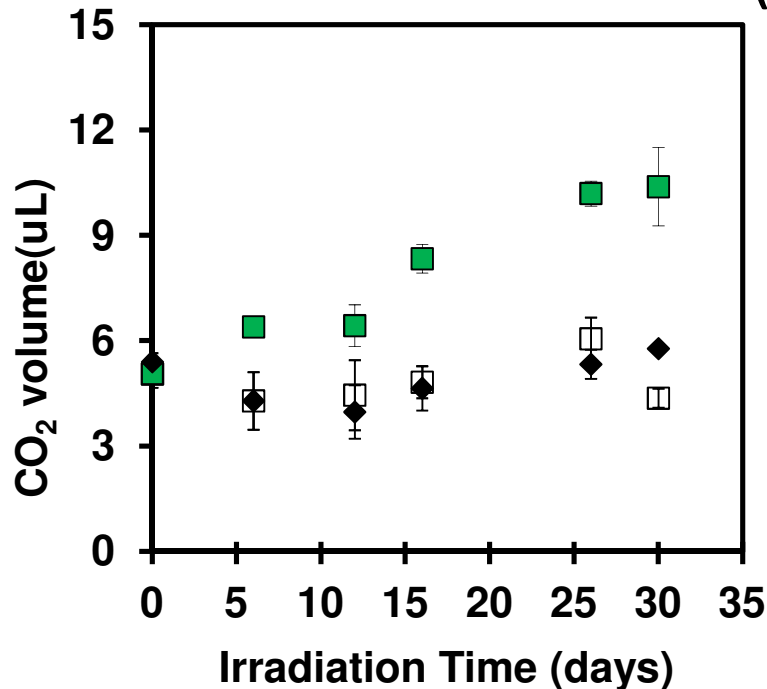
98 days irradiation
Surfactant-free experiment

Data provided by:
Julie Bitter and Howard Fairbrother (JHU)

Reactions during Indirect Photolysis of CNTs with Hydroxyl Radical

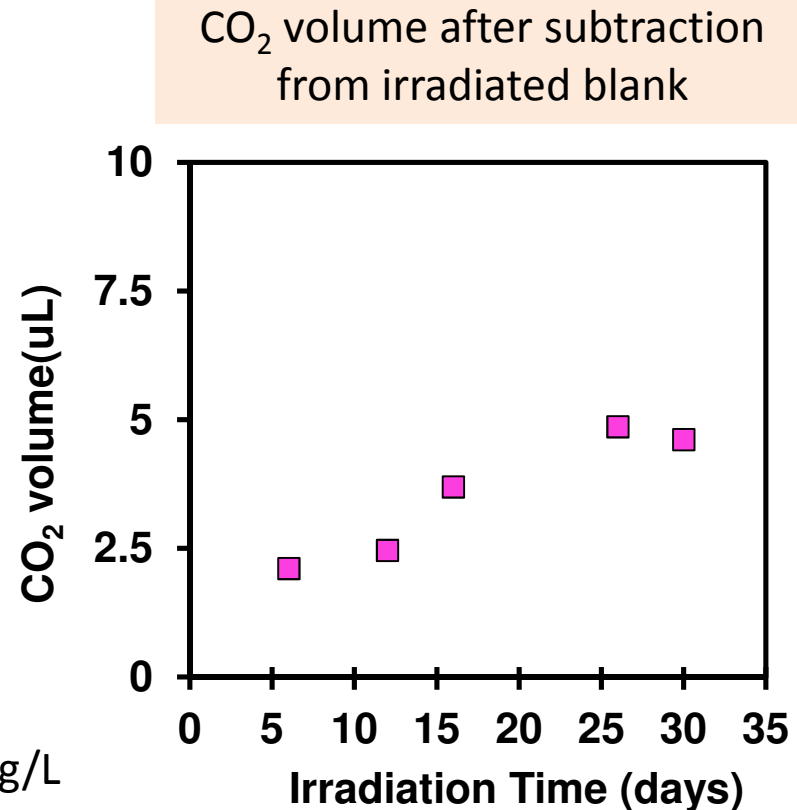


Carboxylated Single-Walled Carbon Nanotubes (Direct)



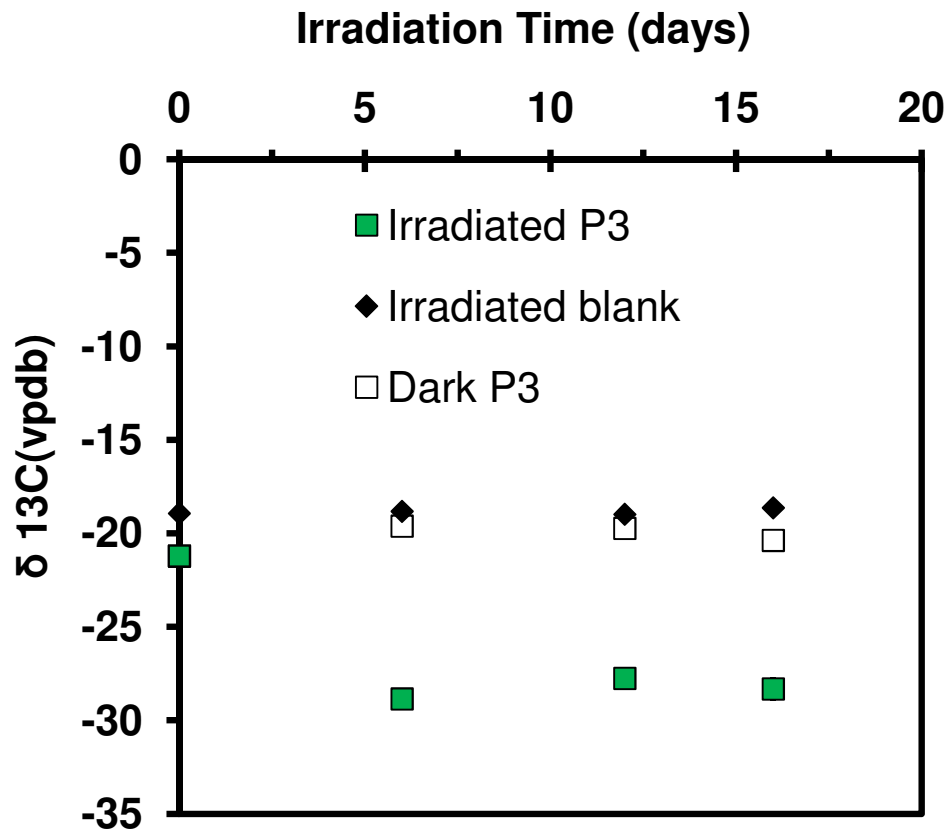
CO₂ volume at pH 7 in lamp light by 45 mg/L SWNT-COOH, (■), blank control (◆) and in the corresponding dark control samples of SWNT-COOH (□)

BeigzadahMilani et al., in draft



TIC₃₀ day = 0.01231 mg
TC₀ = 0.45 mg (in 10 mL)
~2.7% of carbon is converted to CO₂

^{13}C Isotope Ratio ($\delta^{13}\text{C}_{\text{sample/PDB}}$)

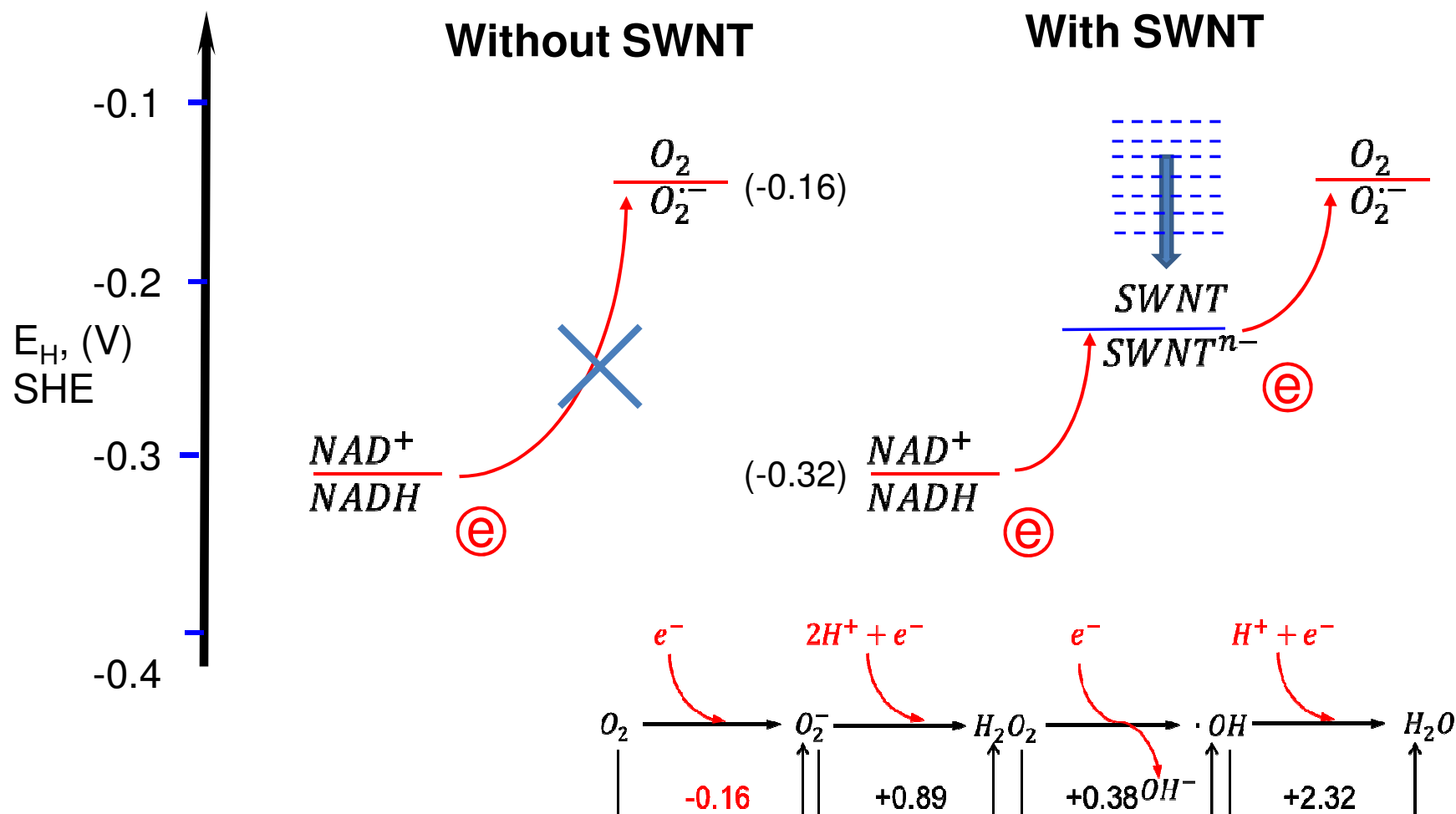


^{13}C ratio in headspace samples for at pH 7 in lamp light by 45 mg/L SWNT-COOH, (■), blank control (◆) and in the corresponding dark control samples of SWNT-COOH (□).

$\delta^{13}\text{C}_{\text{sample/PDB}}$ for original C_{60} powder is about 33.86;
 $\delta^{13}\text{C}_{\text{sample/PDB}}$ for air sample is about -14.

Dark Reactions of Carboxylated SWNTs

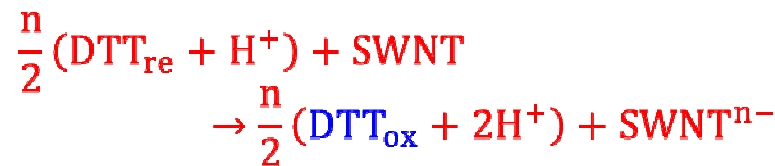
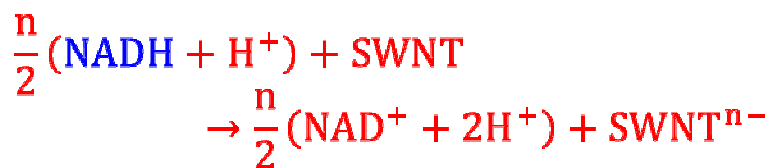
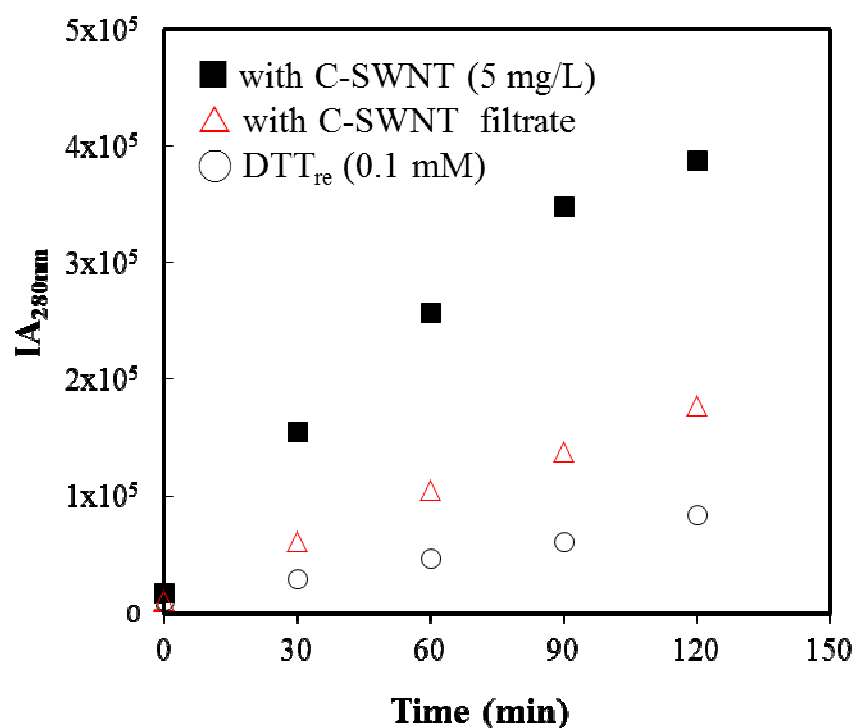
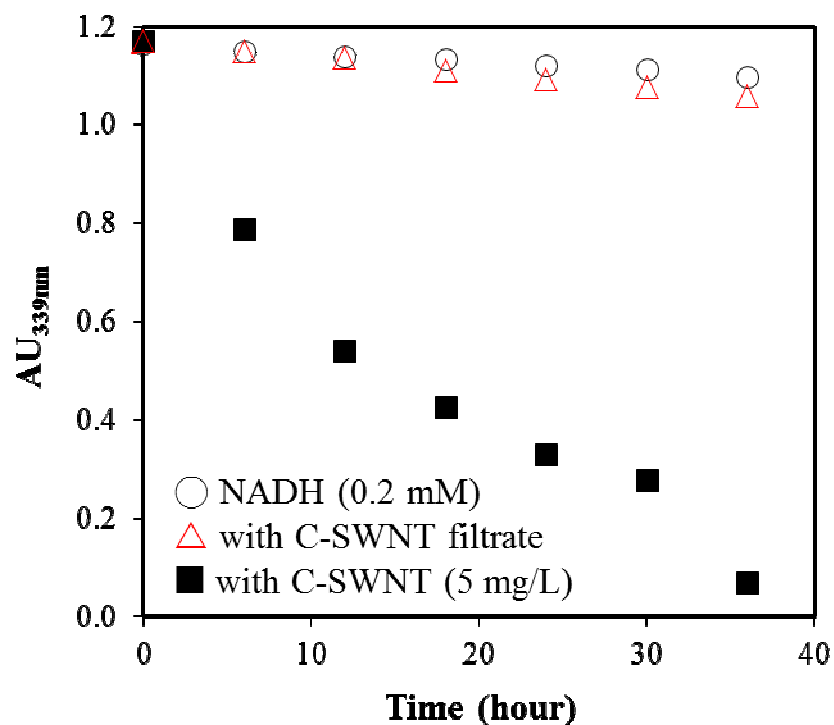
Redox level equilibration of NADH, SWNT, O₂



Hsieh, Hsin-Se, Renren Wu, Chad T. Jafvert, "Light-Independent Reactive Oxygen Species (ROS) Formation through Electron Transfer from Carboxylated Single-Walled Carbon Nanotubes in Water", in press, *Environ. Sci. Technol.*, 2014.

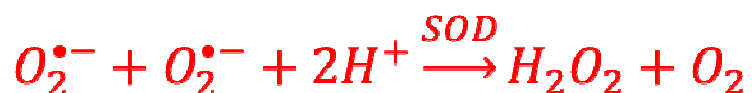
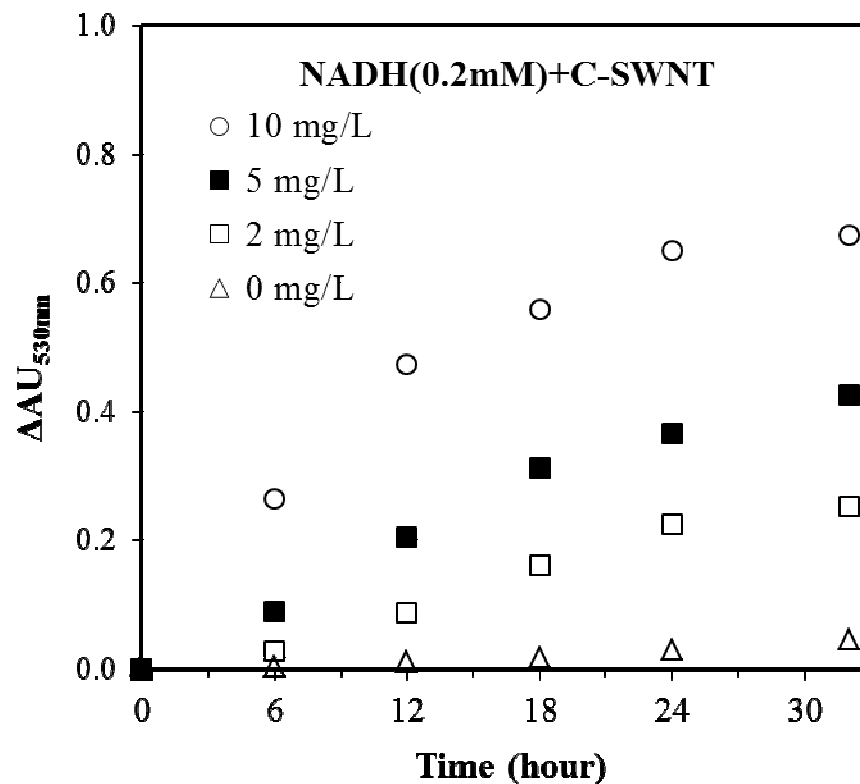
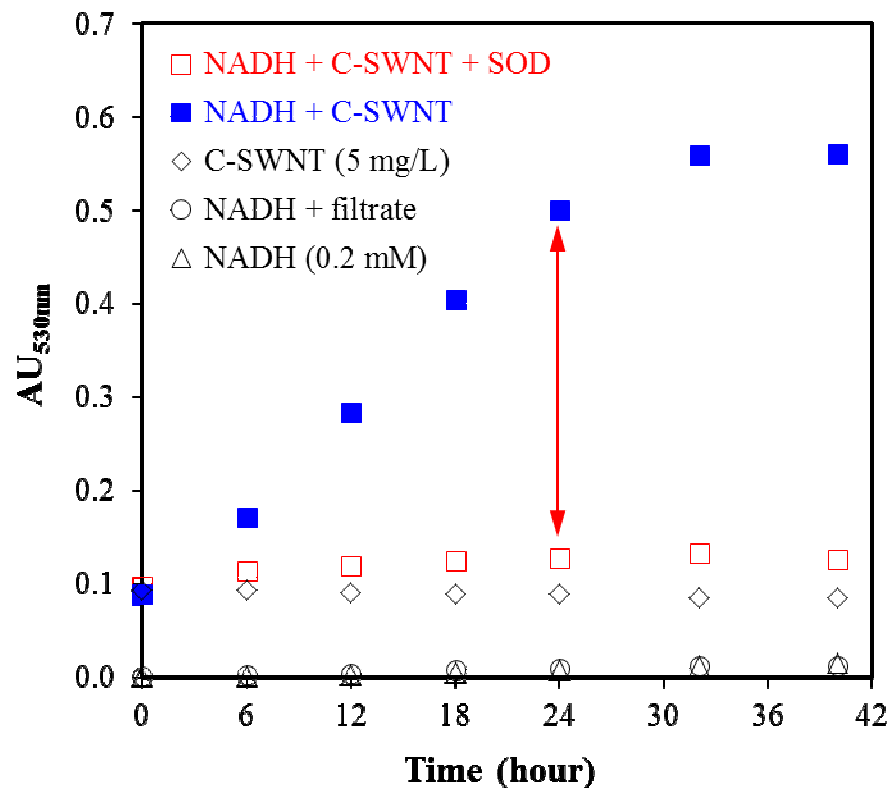
Oxidation of Electron Donors by C-SWNT

C-SWNT = Carboxylated SWCT



$O_2^{\bullet -}$ Production in C-SWNT Suspensions

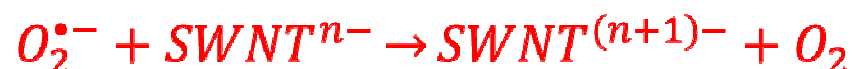
NADH as an Electron Donor



Dose-dependence of C-SWNT
to NBT formazan

Next Step (Reaction of superoxide anion)

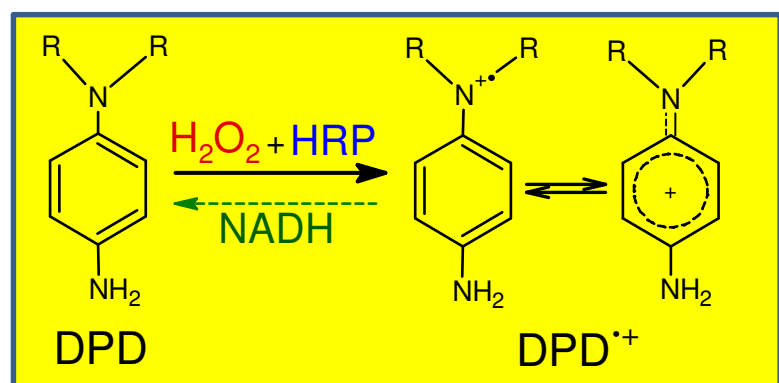
Route 1: scavenged by SWNT



Route 2: disproportionation

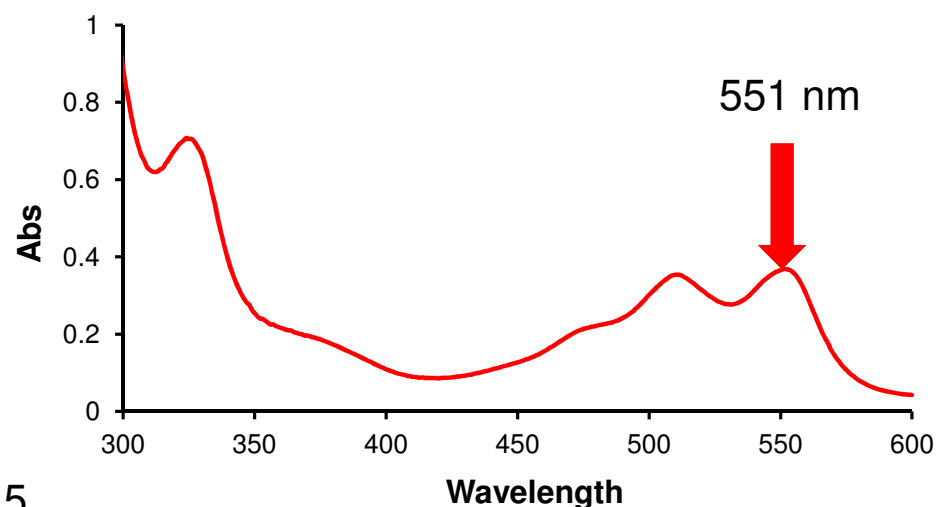


Measurement of H_2O_2 concentration in NADH solution

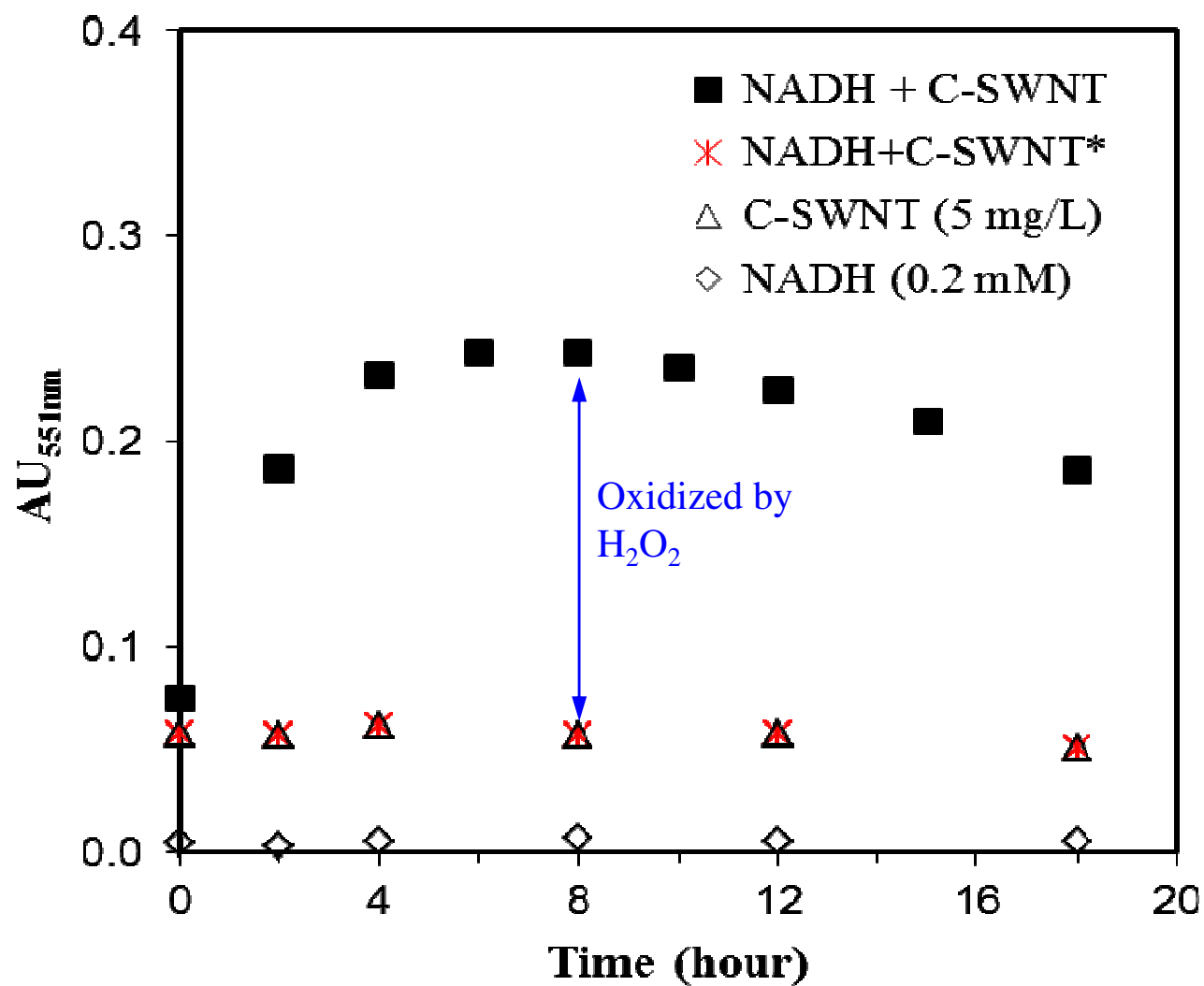


DPD : *N,N*-Diethyl-*p*-phenylenediamine

1. In-solution concentration
(not accumulative)
2. No interference of scavengers



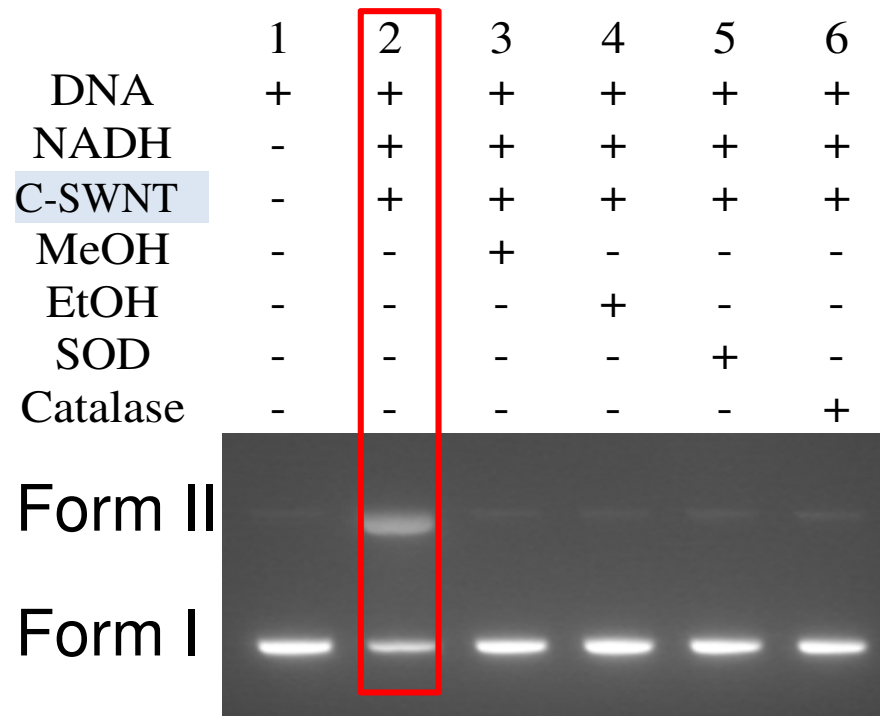
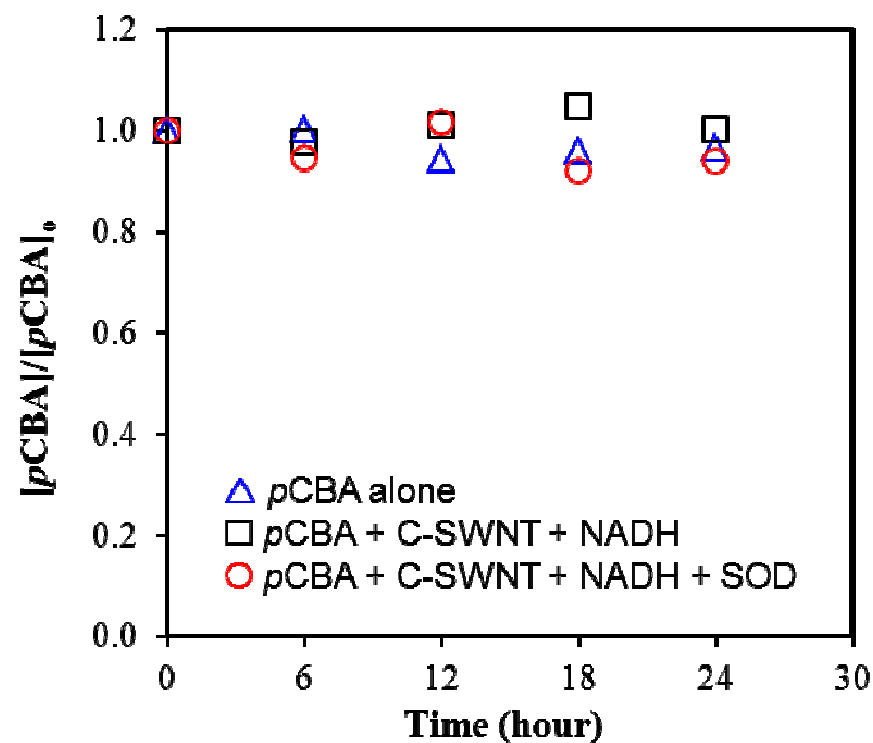
[H₂O₂] in C-SWNT Suspensions w/NADH



Catalase was used to quench H₂O₂ before dosing DPD, HRP

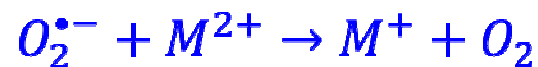
DNA-Cleaving Activity in C-SWCNT/NADH (pBR322 DNA)

No evidence of $\cdot\text{OH}$ by using
*p*CBA (2 μM) as an scavenger

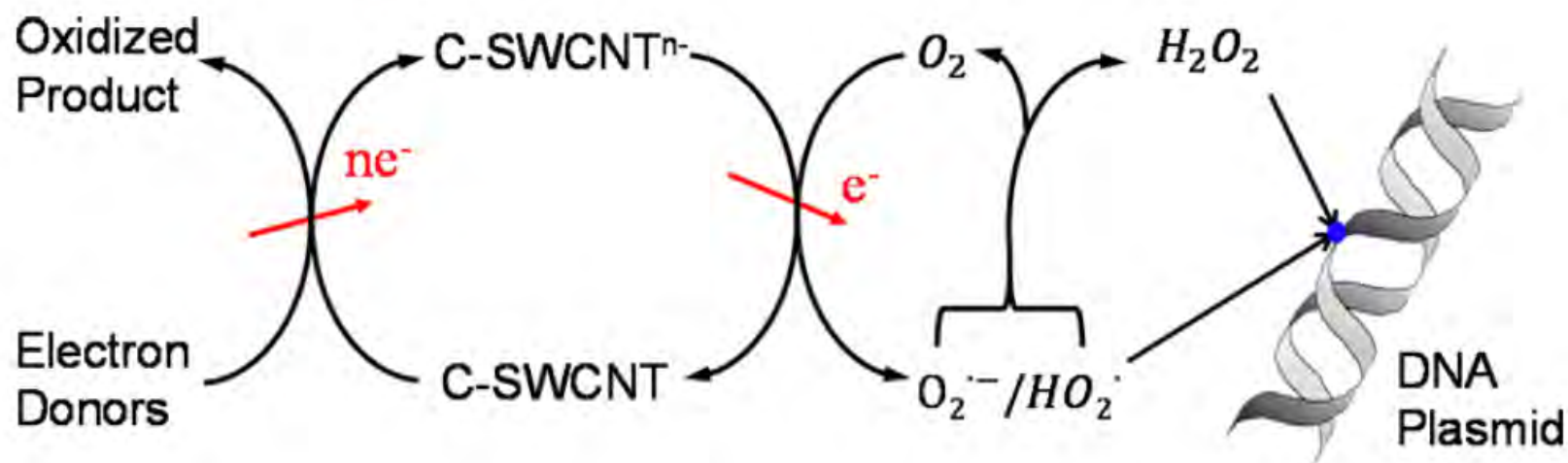


Gel image after 5-hr incubation

MeOH, EtOH $\rightarrow \cdot\text{OH}$ (but not $\text{O}_2^{\bullet-}$)
 Catalase $\rightarrow \text{H}_2\text{O}_2$ to $\text{H}_2\text{O} + \text{O}_2$
 SOD $\rightarrow \text{O}_2^{\bullet-}$ to H_2O_2



Scheme 1. Proposed Mechanism for C-SWCNT to Shuttle Electrons to O_2 , Producing Reactive Oxygen Species and Subsequent DNA Cleavage



Hsieh, Hsin-Se, Renren Wu, Chad T. Jafvert, "Light-Independent Reactive Oxygen Species (ROS) Formation through Electron Transfer from Carboxylated Single-Walled Carbon Nanotubes in Water", in press, *Environ. Sci. Technol.*, 2014.

