

Photochemical and Fungal Transformations of Carbon Nanotubes in the Environment

EPA Grant 83485801

PIs: **Chad T. Jafvert¹, Timothy Filley¹, Howard Fairbrother²**

¹Purdue University and ²Johns Hopkins University

Transformations of carbon nanotubes (CNTs) in the environment are likely to be dominated by abiotic and extracellular microbial processes. Consequently, we are investigating photochemical and fungal mediated transformations of CNTs.¹ Photochemical processes investigated include both direct and indirect photochemical reactions under solar spectrum light, and under shorter wavelength UV light ($\lambda = 254$ nm) to inform us on overall CNT reactivity. Additionally, some dark reactions involving CNTs have been investigated.

Unfunctionalized single walled carbon nanotubes (SWCNTs) are much less reactive under sunlight than functionalized SWCNTs. As a result, we have investigated indirect photochemical reactions of these materials. It is well known that very low ($\approx 10^{-15}$ M) concentrations of hydroxyl radicals occur in many natural waters due to photochemical reactions involving humic acids and other naturally occurring aqueous substances. As a result, we have used solar irradiation of hydrogen peroxide as a way to produce low steady-state concentrations of hydroxyl radicals to study indirect photochemical reactions of unfunctionalized SWCNTs in water. Unfunctionalized SWCNT containing a high fraction of semiconducting (6, 5 chirality) tubes were dispersed in aqueous solutions containing sodium dodecyl sulfate (SDS) and hydrogen peroxide (H_2O_2), and exposed to light from 300-410 nm. Upon irradiation, the ultraviolet and visible absorbance of the solutions decreased, an increase in the Raman I(D) band relative to the I(G) band occurred, and the near infrared fluorescence decreased, all indications that photochemical transformation of the unfunctionalized nanotubes occurred due to the reaction with hydroxyl radicals ($\cdot OH$). Additional experiments in the absence of the surfactant also showed a decrease in the fluorescence signals after 68 and 93 days.

Aqueous suspensions of carboxylated single-walled carbon nanotubes undergo direct photochemical reaction in sunlight. In aqueous suspensions of this material alone (i.e., in the absence of surfactant), there is evidence that the reactive oxygen species (ROS) singlet oxygen (1O_2), superoxide anion ($O_2^{\cdot -}$), and $\cdot OH$ occurs upon irradiation with light within the solar spectrum.^{2,3} Therefore, potential photo-mineralization as well as changes in functional group composition are currently under investigation.

Investigations into the effect of ultraviolet (UV) radiation ($\lambda = 254$ nm) on the fate of oxidized multi-walled carbon nanotube (O-MWCNT) were undertaken using various microscopic and spectroscopic techniques. Absorbance and particle size measurements were employed to monitor the stability of O-MWCNT suspensions while undergoing irradiation of solutions at different pH and ionic strengths. XPS, TEM, and Raman were used to characterize chemical and physical transformations imparted to the CNTs as a result of irradiation. Results show that exposure to 254 nm light causes colloidal O-MWCNTs to become unstable and aggregate in a single photon process at all solution conditions examined. Particle instability was enhanced at low pH and ionic strengths but was independent of the dissolved oxygen concentration. XPS indicated that this destabilization is due to a loss of surface oxygen, which we believe to be the result of a

photo-reduction process where the UV light absorbed is of sufficient energy to break C-O bonds of assorted oxygen-containing functional groups. However, this transformation proceeds in the absence of any significant mass loss or changes in the physical O-MWCNT structure.

In a new initiative as part of this project, we have begun to explore how the inclusion of carbon nanotubes impacts the stability of polymer matrices towards UV irradiation. Photodegradation of nanocomposites is important because it is known that many polymeric materials transform in the presence of UV and visible light. Nanocomposites of polystyrene (PS) containing pristine multi-walled nanotubes were prepared by solution blending and then studied. Mass loss data was collected to track the nanoparticle's ability to accelerate or retard the degradation of the polymer into which it is embedded. Unfunctionalized MWCNTs in PS (p-MWCNT-PS, 0.5% w/w) were irradiated in a ~100 mM hydrogen peroxide/water solution with UVA light (350 nm). Again, the light at this wavelength is energetic enough to cleave the peroxide and generate hydroxyl radicals which may then degrade the polymer or CNTs. Results from this study suggest that in a radical rich environment, the p-MWCNTs may retard the degradation of the PS.

In experiments designed to probe potential dark reactions involving CNTs, the formation of ROS in aqueous suspensions of carboxylated SWCNTs, with the biological reducing agent NADH added as an electron donor, is being investigated. In these suspensions, it appears that the SWCNTs shuttle electrons from NADH to molecular oxygen, forming $O_2^{\cdot-}$, which in turn forms H_2O_2 , which accumulates in solution. Experiments with supercoiled DNA (pBR322) added to these suspensions, shows that the generation of $O_2^{\cdot-}$ and H_2O_2 can result in cleavage of one of the DNA coils. These results suggest that carbon nanotubes can play a role in ROS generation even under dark conditions.

Regarding experiments with CNTs and fungal species, a study was completed to test the enzymatic response of cultured saprotrophic white-rot fungi, *Trametes versicolor* and *Phlebia tremellosa*, to various SWCNTs under different media conditions.⁴ The nanomaterials examined represented a range of SWCNTs synthesized by the same method, and include unpurified (AP-SWCNT), purified and unfunctionalized (P2-SWCNT), and purified and carboxylated (P3-SWCNT) SWCNTs. Figure 1 shows that the unpurified AP-SWCNT and carboxylated P3-SWCNT promoted significant changes in the activity of the oxidative enzymes, laccase and peroxidase, by both white-rot fungi used in this study. The addition of the purified but unfunctionalized P2-SWCNT did not significantly alter enzyme activity. Analysis of residual metals released from the SWCNTs into the media indicated a significant leaching of the metals from unpurified tubes with subsequent fungal uptake, but at levels below those toxic to fungi. Movement of metal into the growth media was not significantly affected by media composition. These results illustrate that the enzymatic response of saprotrophic fungi exposed to carbon nanomaterials is complex, depending not only on the SWCNT surface chemistry, but also on the media composition and fungal species.

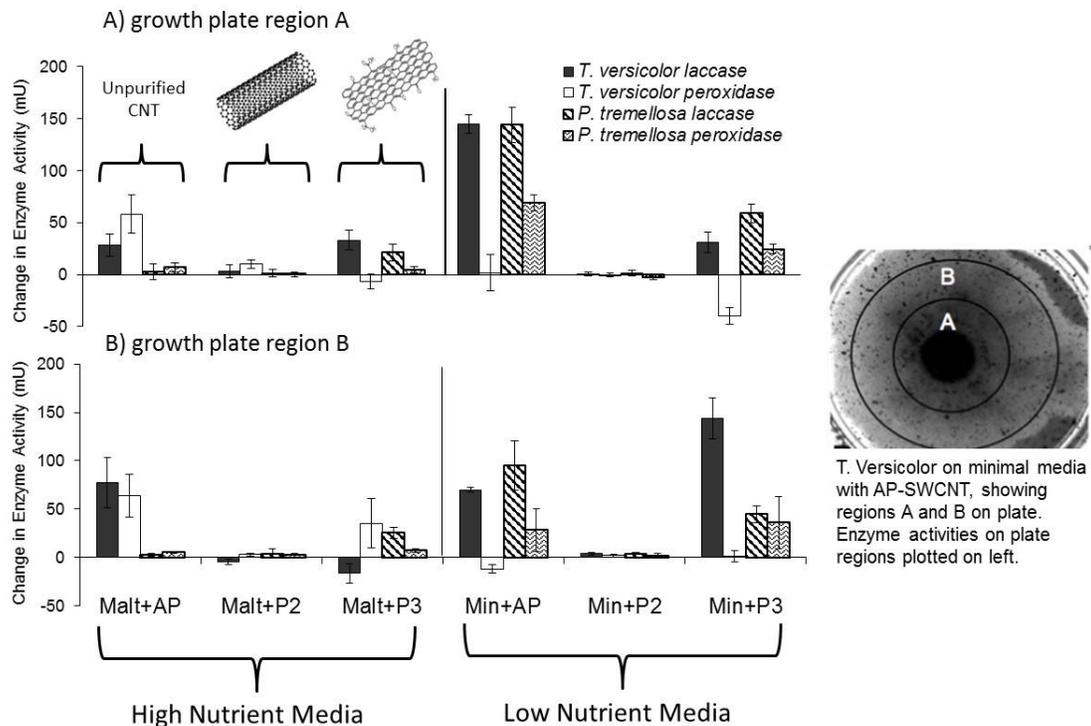


Figure 1. Changes in laccase and peroxidase enzyme activity in cultures of *T. versicolor* and *P. tremelloso* exposed to carbon nanotubes.

References

- [1] For further information about this project, email jafvert@ecn.purdue.edu
- [2] 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* 49, (15), 5099-5106.
- [3] Chen, C.-Y.; Jafvert, C. T., Photoreactivity of Carboxylated Single-Walled Carbon Nanotubes in Sunlight: Reactive Oxygen Species Production in Water. *Environmental Science & Technology* 44, (17), 6674-6679.
- [4] Timothy D. Berry, Timothy R. Filley, Robert A. Blanchette. Enzymatic responses of cultured white-rot fungi to exposure of electric arc produced single-walled carbon nanotubes, *under review*.