ABSTRACT

BeigzadehMilani, Somayeh. Ph.D., Purdue University, May 2015. Environmental Photochemistry of SWCNTs in Aquatic System and Potential Extraction and Purification of Pristine SWCNTs from Soil Matrix. Major Professor: Chad T. Jafvert.

Carbon nanotubes (CNTs) are a class of engineered nanoparticles, composed of an array of sp^2 carbon atoms arranged as fused benzene rings. Due to their exceptional electrical, mechanical, and physical properties, CNTs find applications in construction, aerospace, and medical industries. In the United States, CNTs already had an annual production of 2,000 tons in 2011. This rate of annual production indicates that CNTs will find their way into the environment, which will result in certain environmental exposure. Yet, there have not been sufficient and definitive studies on the health and environment effects of CNTs. For example, additional information regarding environmental transformation pathways is required to better evaluate the environmental and health consequences of these materials. Because photochemical transformation is a potentially important transformation pathway of both unfunctionalized single-walled carbon nanotubes (SWCNTs) and carboxylated SWCNTs (CSWCNTs), this process was investigated in this study. Results show that unfunctionalized SWCNTs can undergo indirect photo-transformation through reactions with hydroxyl radicals (produced from hydrogen peroxide), even in the absence of surfactants, which are often added to disperse the unfunctionalized tubes in water. Evidence for transformation includes UV-VIS and Near Infrared Fluorescence (NIRF) fading, and an increase in defects (sp^3 carbon), as observed through Raman analysis. While more rapid fading occurred under light, changes in the fluorescence of the SWCNTs also occurred in dark samples, suggested some metal-catalyzed Fenton's reaction was occurring in the absence of light.

Although direct photochemical transformation of unfunctionalized SWCNTs is very slow, direct photochemical transformation of aqueous suspensions of CSWCNTs occurs. Headspace analysis on lamp-light irradiated CSWCNT suspensions showed 2.69% of the carbon was mineralized within 30 days. The stable isotope composition of the SWCNTs and of the headspace CO_2 shows that the CO_2 originated from the SWCNTs. XPS analysis, coupled with chemical derivatization of specific oxygen containing functional groups, showed an increase in oxygen content after 60 days under sunlight exposure. Additionally, the wavelength dependency of reactive oxygen species (ROS) generation by CSWCNT was examined under 400- and 280-nm wavelength cutoff filters in sunlight. The aqueous colloidal dispersions of CSWCNTs generated ROS, including: Singlet oxygen ($^1O_2$), superoxide anion ($O_2^{\cdot-}$), and hydroxyl radicals (·OH) under the 280-nm cutoff filter, whereas there was a much slower rate of formation of singlet oxygen ($^1O_2$) and superoxide anion ($O_2^{\cdot-}$) under the 400-nm filter, with no measurable hydroxyl radicals (·OH) produced.

To be able to investigate the fate and transport of CNTs in the environment, it is necessary to develop methods for carbon nanotube isolation (i.e., extraction), characterization, and possibly quantification

from environmental samples. To this end, the potential to use solvent extraction for removing SWCNTs from sand (50+70 mesh) and three types of soil with different characteristics (e.g., Tracy, Drummer, and Clermont) was investigated. Extraction with 1,2-dichlorobenzene (DCB) under high power sonication was shown to have an accumulative extraction efficiency of more than 90% after four sequential extractions. To purify the SWCNTs from the co-extracted humic material, density gradient ultracentrifugation (DGU) was tested using two different commercially available unfunctionalized SWCNTs.