

# Photo-induced interactions between SWCNTs and oxygen

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We will report new investigations of photophysical and photochemical interactions involving single-walled carbon nanotubes (SWCNTs) and oxygen. These processes differ from our earlier discovery that SWCNTs can be covalently doped with O atoms through reaction with oxygen's reactive allotrope, ozone (O<sub>3</sub>) [1]. A fully reversible, non-covalent interaction of aqueous surfactant-coated SWCNTs with dissolved O<sub>2</sub> is revealed by partial quenching of the nanotube fluorescence [2]. The extent of this quenching is found to vary with surfactant coating, reflecting how completely the SWCNT surface is protected. When the SWCNTs are suspended by single-stranded DNA oligomers, the extent of fluorescence quenching reveals selective affinities between specific ssDNA sequences and specific SWCNT structures. By contrast, we have found that a covalent photochemical reaction with dissolved oxygen occurs when SWCNTs are strongly irradiated at their E<sub>11</sub> absorption peaks. The result is persistent and spectrally localized fluorescence quenching resulting from an optically directed photochemical reaction with the SWCNT sidewall. This process holds promise for allowing the optical properties and possibly the composition of mixed SWCNT samples to be tailored by targeted photochemistry. Recent evidence will also be presented that SWCNT triplet excited states can be formed through solution-phase energy transfer from O<sub>2</sub> in its singlet excited state. The key observation is weak delayed SWCNT fluorescence, which apparently comes from thermal excitation of long-lived SWCNT triplet excitons to emissive singlet states. Finally, we will show novel fluorescence signatures from ssDNA-wrapped SWCNTs exposed to singlet O<sub>2</sub>. This process leads to a covalent sidewall reaction involving one nucleotide base in the ssDNA. The resulting reaction product displays intense nanotube fluorescence with (*n,m*)-dependent spectral shifts and broadening, modified absorption spectra, and intriguing temperature dependences. This reaction class may offer a new path for chemically modifying SWCNT optical properties.

[1] S. Ghosh, S. M. Bachilo, R. A. Simonette, K. M. Beckingham, R. B. Weisman, *Science* **330**, 1656 (2010).

[2] Y. Zheng, S. M. Bachilo, R. B. Weisman, *J. Phys. Chem. Lett.* **8**, 1952 (2017).