Supporting Information

Photoreactivity of Unfunctionalized Single-Wall Carbon Nanotube Involving Hydroxyl Radical: Chiral Dependency and Surface Coating Effect

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Text S1. SWCNT concentration standardization by the UV-visible-NIR absorbance spectra

The tip sonicated sample of SWCNT in the aqueous surfactant was immediately diluted sequentially to give a series of samples with varied SWCNT concentrations. The tip sonicated sample was not centrifuged so that the added SWCNT material was all in suspension. To determine the light attenuation coefficient, α, the UV-visible-NIR absorbance spectra of SWCNT samples were recorded immediately after dilution to avoid SWCNT precipitation. The absorbance at 891 nm reflective of the SG65 SWCNT's baseline absorbance are plotted as a function of concentration, yielding a straight line with a slope of 0.022 L/mg·cm (i.e., α). The value is consistent with that reported in an earlier work (α = 0.020 L/mg·cm).

A recent work by Khripin et al. indicates that the light absorbance of SWCNT is dependent on the length of SWCNT and that the SWCNT quantitation using baseline absorbance could result in up to 40% of error.[1] While there are likely errors in the SWCNT concentration measurement using the baseline absorbance, our goal was to standardize the amounts of SWCNTs added to the experiments so they are comparable, rather than to accurately determine them. Nevertheless, the uncertainty in the SWCNT concentration is canceled out during the kinetic analysis in obtaining the pseudo first-order rate constant (k_{expt}) of SWCNT's PL quenching, where the amount of unreacted SWCNT (as measured by its PL intensity) is normalized by the initial amount of SWCNT added.
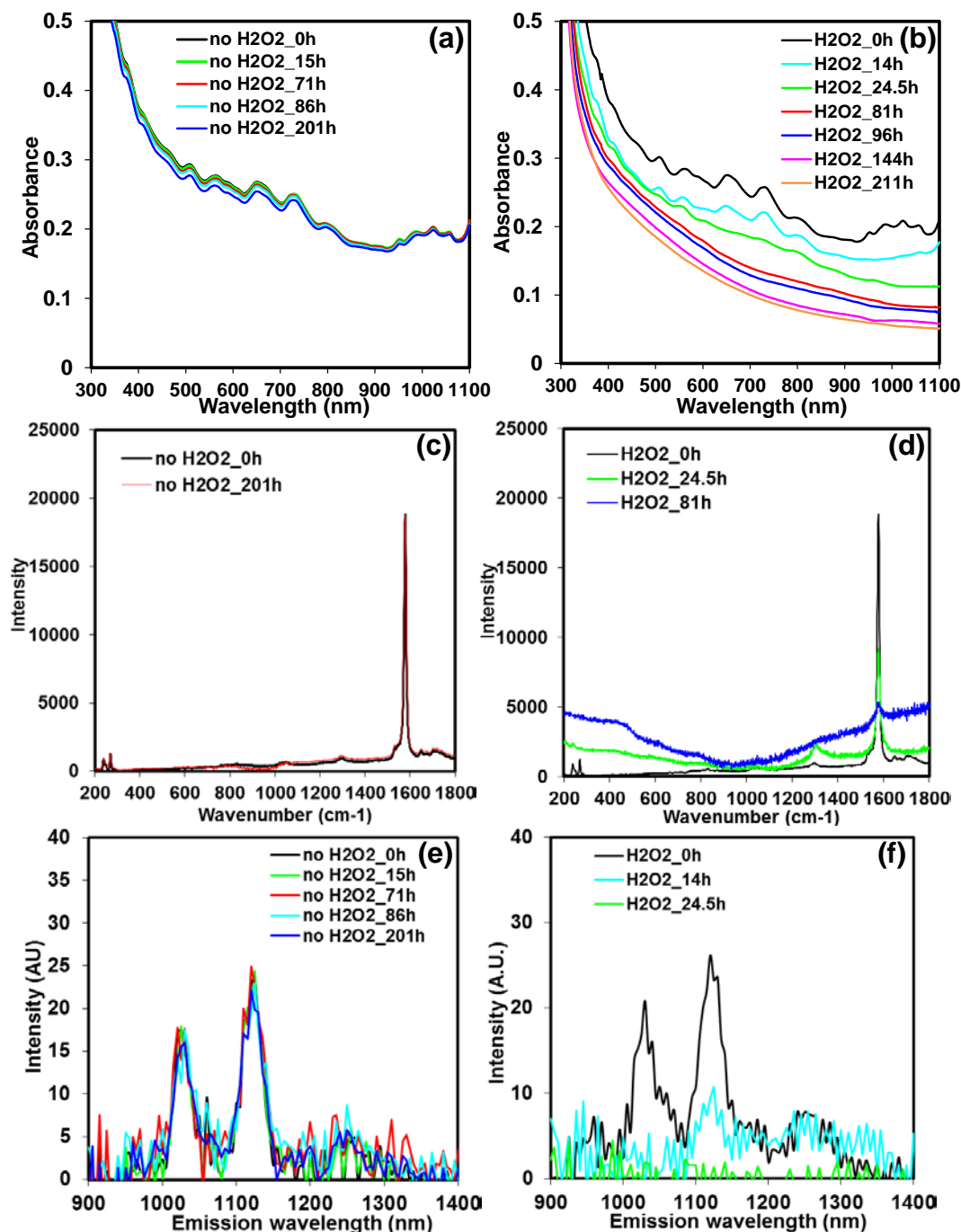
Figure S1. Phototransformation of HiPco SWCNT as indicated by UV-visible-NIR absorbance in samples (a) without H_2O_2, or (b) with 100 mM H_2O_2, by Raman spectroscopy in samples (c) without H_2O_2, or (d) with 100 mM H_2O_2, and by NIRF in samples (e) without H_2O_2 or (f) with 100 mM H_2O_2. HiPco SWCNT sample was dispersed in 1% SDS. The excitation wavelength was 640 nm for the NIRF analyses. The spectra are the averages of at least two replicate samples.
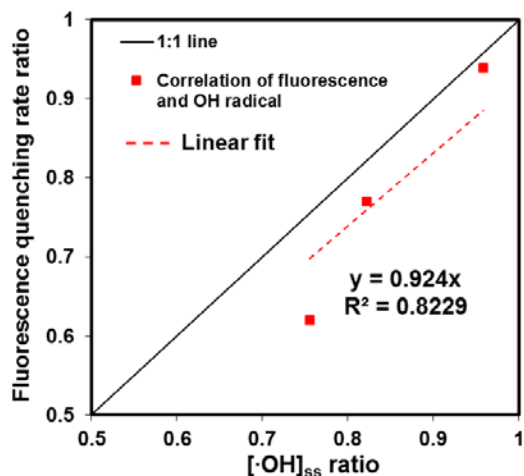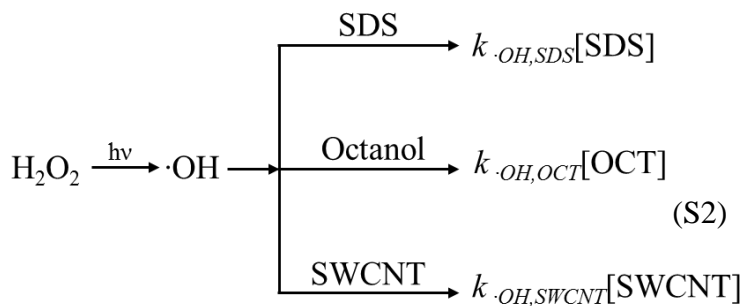
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Figure S2. Effect of octanol (as ·OH quencher) addition on the reaction of SG65 SWCNT and ·OH, showing the correlation of the reduction in steady state ·OH concentration and the decrease in fluorescence quenching rate. The $[·OH]_{ss}$ ratio indicates the steady state ·OH concentrations in the presence of octanol to that without octanol added; fluorescence quenching rate ratio indicates the pseudo 1st-order rate constants of PL quenching in the presence of octanol to that without octanol added. H_2O_2 concentration was 100 mM. SWCNT was in 1% SDS. The kinetic analysis is presented in text S2.

Text S2. Kinetic analysis of ·OH reaction in the SWCNT-SDS-octanol-system

Previous kinetic studies of reactions mediated by hydroxyl radicals, ·OH, under dilute aqueous conditions have shown that the steady-state concentration of ·OH ($[·OH]_{ss}$) is given by the rate at which the ·OH is produced ($r_{·OH}$) divided by the sum of pseudo first-order rate constants ($k_{·OH,Ci}[C_i]$) for the reactions by which ·OH becomes consumed in the system:

$$[· OH]_{ss} = \frac{r_{·OH}}{\sum k_{·OH,C_i}[C_i]} \qquad\qquad (S1)$$

where $k_{·OH,Ci}$ is the second-order rate constant for the reaction of ·OH with chemical compound C_i present in the system; $[C_i]$ is the molar concentration of compound C_i.   The formation rate ($r_{·OH}$) in the present study is proportional to the rate of direct photolysis of H_2O_2, the photochemical source of ·OH. Addition of the ·OH scavenger, 1-octanol, slowed the photoreaction of SWCNT in the presence of H_2O_2. As illustrated in eq S2, the retarding effect of octanol involves its reaction with ·OH at the rate of $k_{·OH,oct}[OCT]$.   Reaction with the surfactant SDS ($k_{·OH,SDS}[SDS]$), another excellent ·OH scavenger,[2] also retards indirect photoreaction of SWCNT.   Reaction of ·OH with H_2O_2 is another potential ·OH sink, but it could be shown that this reaction is too slow to be a significant factor in this kinetic analysis. Reaction of ·OH with the SWCNT is another, albeit minor, reaction that is relevant to the assessment of its reaction kinetics. As described below, this reaction likely involves multiple sites for ·OH attack that have different rate constants.   However, the SWCNT concentration is sufficiently low that its reaction rate with ·OH in this system is much smaller than those with octanol and SDS and hence SWCNT has little effect on $[OH]_{ss}$.

$$H_2O_2 \xrightarrow{h\nu} ·OH \longrightarrow
\begin{array}{l}
\xrightarrow{\text{SDS}} k_{·OH,SDS}[SDS] \\[6pt]
\xrightarrow{\text{Octanol}} k_{·OH,OCT}[OCT] \\[6pt]
\xrightarrow{\text{SWCNT}} k_{·OH,SWCNT}[SWCNT]
\end{array}
\qquad (S2)$$

Rate constants of reactions for ·OH with octanol ($k_{·OH,oct} = 6 \times 10^9$ $M^{-1}s^{-1}$) and SDS ($k_{·OH,SDS} = 8.2 \times 10^9$ $M^{-1}s^{-1}$) have been previously measured.[2]

To quantify production rates and steady-state concentrations of ·OH, rates of its reaction with the added probe molecule, pCBA, were determined. The experiments were performed in a way that a simple second-order rate law was observed in which the rate of pCBA decay was first order in both concentration of pCBA and ·OH:

$$-\frac{d[pCBA]}{dt} = k_{·OH,pCBA}[·OH]_{ss}[pCBA] \qquad (S3)$$

where $[·OH]_{ss}$ is the "steady-state" concentration of ·OH and $k_{pCBA,·OH}$ is the second-order rate constant for reaction of ·OH with pCBA, which is known to be 5.2×10^9 $M^{-1}s^{-1}$.[2] Under the conditions of our study, the concentration of pCBA was extremely dilute (1.5 µM) and thus low enough not to significantly change $[·OH]_{ss}$. Eq S3 integrates to:

$$-\ln\frac{[pCBA]}{[pCBA]_0} = k_{·OH,pCBA}[·OH]_{ss}t \qquad (S4)$$

Therefore, the logarithm of the relative residual concentration of pCBA declines linearly with time with a slope of $k_{pCBA,·OH}[·OH]_{ss}$ (apparent first-order kinetics). $[·OH]_{ss}$ then was calculated directly from the pseudo first-order rate constant for loss of pCBA using the known value for reaction of $k_{·OH,pCBA}$. All kinetic experiments with pCBA applied in this study yielded very good first-order plots.

Using this approach, it was determined that $[·OH]_{ss}$ was 2.44×10^{-15} M, 2.30×10^{-15} M, 2.0×10^{-15} M, and 1.80×10^{-15} M, respectively, in 1.0% aqueous SDS (0.035 M), in 1.0% SDS with added 0.0020 M octanol, in 1.0% SDS with added 0.010 M octanol, and in 1.0% SDS with added 0.0150 M octanol.

Using the $[·OH]_{ss}$ with concurrently measured pseudo first-order rate constants, k_{expt}, for the loss of the band-gap fluorescence of SG65 SWCNT, the operationally defined second-order rate constant, $k_{·OH,SWCNT}$, for reaction of this SWCNT with ·OH was computed using eq. S5.

$$k_{·OH,SWCNT} = \frac{k_{expt}}{[·OH]_{ss}} \qquad (S5)$$

Kinetic analysis for data presented in Figure S2.

Re-arranging eq. S5 yields:

$$k_{expt} = k_{\cdot OH,SWCNT}[\cdot OH]_{ss} \qquad (S6)$$

In the absence of octanol quencher, eq. S6 is expressed as:

$$k^o_{expt} = k_{\cdot OH,SWCNT}[\cdot OH]^o_{ss} \qquad (S7)$$

where $k^o_{expt,OCTi}$ and $[\cdot OH]^o_{ss,OCTi}$ represent the measured pseudo first-order rate constants of fluorescence quenching and steady state ·OH concentrations in the absence of octanol.

In the presence of octanol quencher, eq. S6 is expressed as:

$$k_{expt,OCT_i} = k_{\cdot OH,SWCNT}[\cdot OH]_{ss,OCT_i} \qquad (S8)$$

where $k_{expt,OCTi}$ and $[\cdot OH]_{ss,OCTi}$ represent the measured pseudo first-order rate constants of fluorescence quenching and steady-state ·OH concentrations in the presence of octanol at varied concentrations.

Dividing eq. S8 by eq. S7 gives:

$$\frac{k_{expt,OCT_i}}{k^o_{expt}} = \frac{[\cdot OH]_{ss,OCT_i}}{[\cdot OH]^o_{ss}} \qquad (S9)$$

Therefore, the ratio (i.e., $k_{expt,OCTi}/k^o_{expt}$ as the y axis in Figure S2) of pseudo first-order fluorescence quenching rate constant in the presence of octanol to that without octanol present is linearly proportional (with a slope of unity) to the ratio (i.e., $[\cdot OH]_{ss,OCTi}/[\cdot OH]^o_{ss}$ as the x axis in Figure S2) of steady-state ·OH concentration in the presence of octanol to that without octanol present.
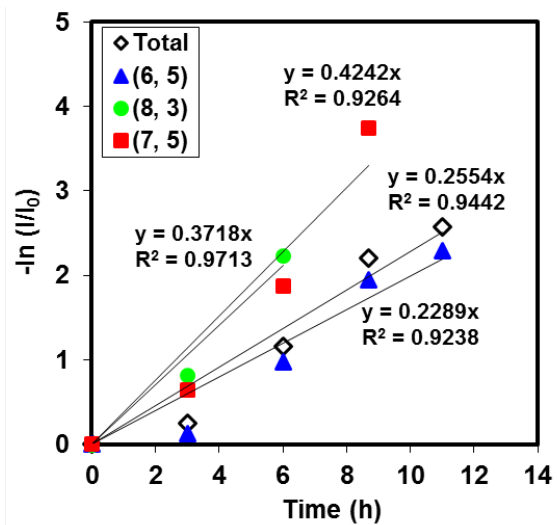
Figure S3. The photoreaction of SWCNTs in the presence of H_2O_2, showing the kinetic traces of each chiral tube and all tubes combined. The reaction kinetic is measured as the photoluminescence intensity of samples reacted over time normalized to that of sample before reaction.

Text S3. Effect of Water Chemistry

We tested several water chemistry parameters on the photoreactivity of SWCNT, including the dissolved O_2 concentration, the presence of Suwannee River humic acid, and the use of a real river water sample collected from the Oconee River in Athens, GA on the photoreactivity of SWCNT without H_2O_2 added. The results are shown in Figure S3-5. The conditions did not change SWCNT's photoreactivity in our experimental time scales.

O_2 removal (by using the N_2 glove box) does not significantly affect the direct photolysis of SWCNT in aqueous 1% SDS dispersions (Figure S3). This is in large contrast to a previous study where N_2-purged SWCNT in aqueous SDS surfactant rapidly reacts within minutes under UV at 254-nm light irradiation (comparing to the sunlight spectrum of 280-800 nm used in our study),[3] suggesting the light wavelength (i.e., photon energy) used plays a role in phototransformation of SWCNT. The slight increase in the PL is consistent with earlier reports showing that degassing SWCNT dispersions could remove the low level of chemically or physically sorbed O_2.[3,4]

The presence of 12 mg C/L SRHA (Figure S4) and the use of Oconee River water (Figure S5) do not significantly effect SWCNT transformation in 63 h and 10 h of sunlight exposure, respectively. Humic substances are well-known ROS generators in sunlit waters. The fact that we do not observe SWCNT transformation could be attributed to the competition of SDS surfactant for ROS and/or the irradiation time not long enough for transformation to occur.
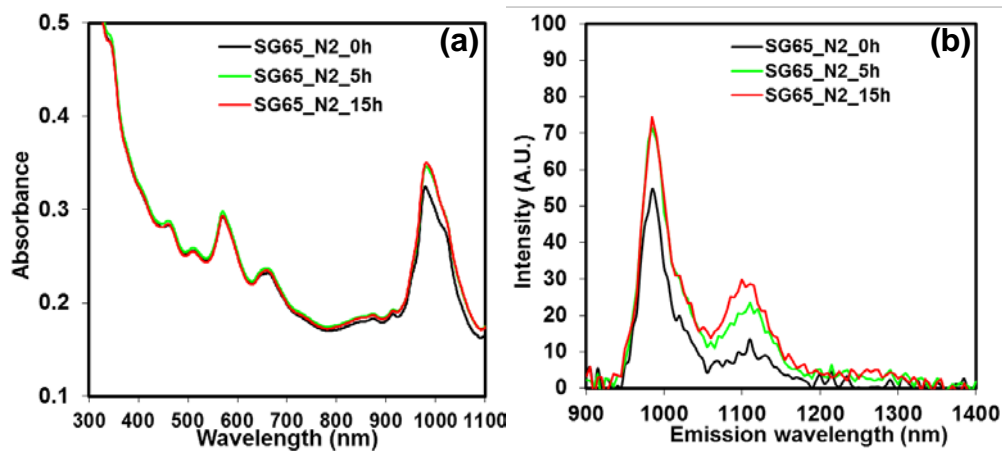
Figure S4. Phototransformation of SG65 SWCNT samples saturated with N_2 without H_2O_2 added under sunlight exposure at pH=7.0, showing the (a) UV-visible-NIR absorbance and (b) NIRF spectra. SWCNT sample was in 1% SDS. The excitation wavelength was 567 nm for the NIRF analyses.
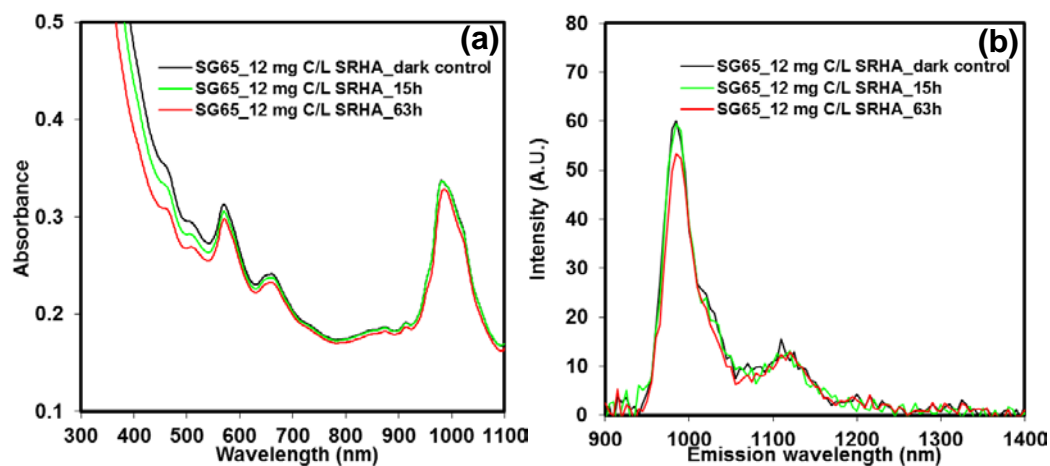
Figure S5. Photoreactivity of SG65 SWCNT in 12 mg C/L Suwannee River humic acid (SRHA) samples, showing the (a) UV-visible-NIR absorbance and (b) NIRF spectra. SWCNT suspensions in 1% SDS were mixed with SRHA solutions to yield samples containing 8.0 mg/L SWCNT and 12.0 mg C/L SRHA with pH of 7.0 (no buffering). The excitation wavelength was 567 nm for the NIRF analyses.
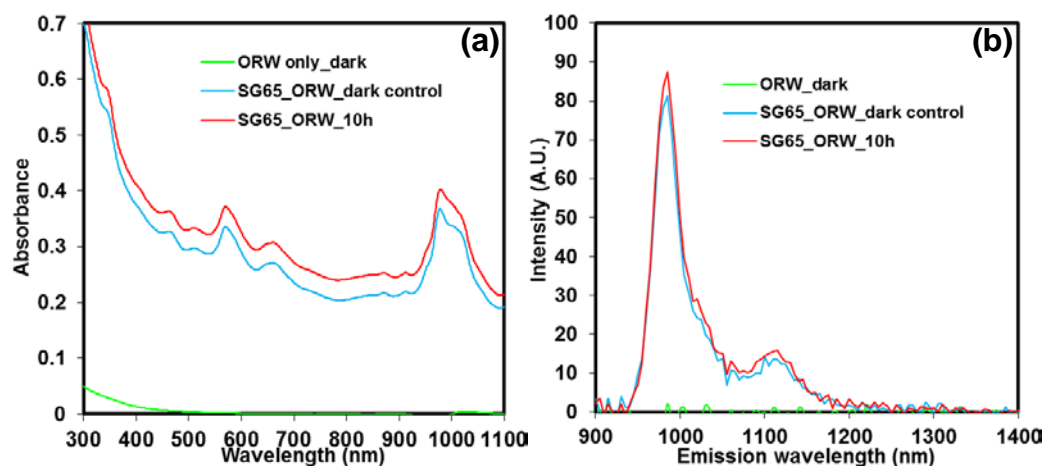
Figure S6. Photoreactivity of SG65 SWCNT in the Oconee River water (ORW) samples, showing the (a) UV-visible-NIR absorbance and (b) NIRF spectra.   SWCNT in 1% SDS was added to ORW samples to reach 8.0 mg/L SWCNT at pH=7.3 (no buffering).   The excitation wavelength was 567 nm for the NIRF analyses.

References

(1) Khripin, C. Y.; Tu, X.; Howarter, J.; Fagan, J.; Zheng, M. Concentration Measurement of Length-Fractionated Colloidal Single-Wall Carbon Nanotubes. *Anal. Chem.* **2012**, *84*, 8733–8739.

(2) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot$OH/$\cdot$O− in Aqueous Solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886.

(3) Alvarez, N. T.; Kittrell, C.; Schmidt, H. K.; Hauge, R. H.; Engel, P. S.; Tour, J. M. Selective Photochemical Functionalization of Surfactant-Dispersed Single Wall Carbon Nanotubes in Water. *J. Am. Chem. Soc.* **2008**, *130*, 14227–14233.

(4) Dukovic, G.; White, B. E.; Zhou, Z.; Wang, F.; Jockusch, S.; Steigerwald, M. L.; Heinz, T. F.; Friesner, R. A.; Turro, N. J.; Brus, L. E. Reversible Surface Oxidation and Efficient Luminescence Quenching in Semiconductor Single-Wall Carbon Nanotubes. *J. Am. Chem. Soc.* **2004**, *126*, 15269–15276.