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Photosensitized Singlet Oxygen Production upon Two-Photon Excitation of Single-Walled Carbon Nanotubes and Their Functionalized Analogs

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Abstract

Single-walled carbon nanotubes (SWNTs) functionalized with -COOH (along with some sulphonation and nitration), and/or modified with chitosan were prepared and tested for their singlet oxygen ($^{1}O_{2}$) production. The emission from $^{1}O_{2}$ observed upon SWNT irradiation at 532 nm was due to a two-photon process, while $^{1}O_{2}$ production via excitation at 355 nm occurred through a conventional one-photon pathway. The relative quantum yield of $^{1}O_{2}$ production at excitation wavelength of 532 nm was found to be 0.00, 0.07-0.13 and 0.24-0.54 for highly-functionalized, partially-functionalized and non-functionalized SWNT samples respectively. The nanotube-mediated generation of $^{1}O_{2}$ may find applications in both targeted destruction of tumor cells and selective degradation of drug molecules. Our research provides a practical approach to modulate the production of reactive oxygen species from SWNTs via surface functionalization/modification.

The unique mechanical, ¹ electrical² and optoelectronic^{3,4} properties of single-walled carbon nanotubes (SWNTs) have attracted considerable attention. Carbon nanotubes do not have a resonant, one-photon transition in a visible or near-infrared spectral region. The two photon absorption (TPA) coefficient $\beta_0 \sim 1.4$ cm/MW and a nonlinear index $\gamma \sim -5.5 \times 10^{-11}$ cm²/W of SWNTs have been determined by femtosecond z-scan technique and theoretical simulations. ⁵ A remarkable feature of this phenomenon is that the probability of a TPA process is proportional to the square of incident light intensity. In effect, visible photons can cause photoreactions in UV absorbing species, and near infrared photons in visible absorbing species. A practical application of TPA in photodynamic therapy is that ¹O₂ photosensitization can be carried out at near-infrared wavelength, where the tissue is significantly more transparent than in the visible region.6⁻⁸ Recent research has revealed an exciting aspect of carbon nanotubes - their ability to produce reactive oxygen species (ROS) upon irradiation, ⁹, 10 which can lead to additional therapeutic applications such as targeted destruction of tumor cells and/or nanotube-mediated drug degradation. In spite of the facts that nonlinear optical techniques have been well established for populating excited states in carbon nanotubes. 11,12 and the surface functionalization/modification can introduce various functional groups for drug

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delivery $^{13-15}$ and diagnostic purpose, $^{15-18}$ the current state of knowledge related to photo induced activities and the nature of photoexcitation in SWNTs for $^{1}O_{2}$ production are rather limited. There are only a few reports related to remarkable reduction in cytotoxic effects upon functionalization, 19,20 nanotube-mediated photooxidation, 14,21 cancer cell death 13 and protein damage. 10

Appropriate chemical functionalization and/or physical modification of nanotubes are critical issues in biomedical applications. They not only enhance the dispersibility of the insoluble tubes leading efficient delivery, and but also allow the incorporation/interaction with other of drug molecules. More importantly, functionalization provides new classes of SWNT-based materials with specific physical and chemical properties including photo activity. Consequently, it is conceivable that all real-world application of nanotubes will involve some level of chemical functionalization. Of particular interest are covalent derivatizations and physical modification, where different functional groups may be attached directly to the nanotube backbone, and nanotubes can be wrapped with polymers, respectively. Another important issue is the presence of residual catalyst on the SWNTs preparations. To date there exist no reports on the effects of either purification or functionalization/modification on $^{1}O_{2}$ generation. The understanding of these issues is of great significance in realizing practical applications of photo excitation and photo activity of carbon nanotubes.

These fundamental issues will be addressed in this paper. First, can singlet oxygen $(^{1}O_{2})$ be formed by the interaction of excited SWNTs with ground state molecular oxygen $(^{3}O_{2})$? Our measurements with time-resolved and steady-state photolysis represents the first direct observation of $^{1}O_{2}$ emission at 1270 nm upon visible excitation of SWNTs, and also demonstrates its dependence on surface functionalization/modification. Second, what is the nature of the UV and visible photoexcitations in SWNTs? We report for the first time that SWNT excitation is a two-photon process at 532 nm, and a one-photon process at 355 nm.

SWNT samples (table 1) were dispersed in $1:1\ D_2O/H_2O$ solutions and illuminated in a pulsed laser beam and/or under visible light in steady-state photolysis. The SWNT surfaces were functionalized with -COOH along with some sulphonation and nitration as previously reported ¹⁷ and/or modified with chitosan (CHIT), an ideal biopolymer for drug delivery (see supporting information). ²² High viscosity solutions of 10% poly(diallyldimethylammonium chloride) (PDDA) were used for obtaining uniform distribution of intrinsic SWNTs that were neither functionalized nor modified (samples 5 and 7). $^{1}O_2$. quenching from PDDA as well as SWNT aggregation in PDDA can be disregarded as Stern-Volmer analysis in D_2O shows no obvious decrease in $^{1}O_2$ signals at 10% PDDA.

Kinetic decay of $^{1}O_{2}$ luminescence at 1270 nm upon 532 nm irradiation was monitored using experimental setup reported previously. 23,24 The signals shown in figure 1 were assigned to $^{1}O_{2}$ phosphorescence on the basis of the following points. First, both kinetics and intensity of the signals were sensitive to the concentrations of oxygen and azide ions (reacting with $^{1}O_{2}$ at a rate constant of 5×10^{8} M $^{-1}$ s $^{-1}$ 25 $^{\circ}$ 26) in the solution. Second, the signal decay was always single exponential. The decay rate constant of $^{1}O_{2}$ (k_{d}) calculated by 1^{st} -order kinetic fitting to $^{1}O_{2}$ phosphorescence decay was found to be $(8.0\pm0.7)\times10^{4}$ s $^{-1}$ in 1:1 D $_{2}O/H_{2}O$ solvent, which lay between the reported values 1.5×10^{4} s $^{-1}2^{7}$ for D $_{2}O$ and 2.4×10^{5} s $^{-1}2^{8}$ for H $_{2}O$. Third, 9,10-dimethylanthracene (DMA) is known to quench $^{1}O_{2}$ chemically only, at a high rate constant, e.g., 2.9×10^{7} M $_{2}O$ s ^{-1}O in CHCl $_{3}O$ Trapping studies with DMA also indicated the formation of $^{1}O_{2}$ upon visible illumination of SWNT (table 2). The conversion of DMA to DMA oxide was monitored by ^{1}H NMR (see supporting information). Our results show that higher conversion yields were observed for underivatized (sample 5) over functionalized SWNTs (sample 3), and for purified (sample 5) over that containing residualiron (sample 7). "Purified" here refers to SWNTs, where the metal and amorphous carbon

content had been reduced by controlled treatment, but the side walls had not been functionalized. 30 CHIT was excluded in steady-state experiments as it may be decomposed by 1 O₂ during long periods of illumination.

Based on photosensitization mechanisms, the production of ROS is usually carried out via type I and/or type II pathways.³¹ A type I mechanism involves hydrogen-atom abstraction or electron-transfer between an excited sensitizer and a substrate, and the subsequent generation of oxygen radicals. A type II mechanism involves the generation of ¹O₂ via energy transfer between excited triplet sensitizer and ³O₂. Foote and co-workers found that the quantum yields of triplet formation for C_{60} and C^{70} were close to unity. ^{32,33} Both C^{60} and C^{70} belong to the same family as carbon nanotubes. The deactivation of triplet state in C_{60} can occur via either type I or type II mechanisms.³²⁻³⁴ Photoinduced nanotube-assisted generation of superoxide and hydroxyl radicals via electron transfer reaction has been evidenced by carbon nanotubes mediated deactivation of proteins. ¹⁰ The lowest triplet energy in carbon nanotubes was recently calculated to be ca. 0.2-0.3 eV lower than the lowest singlet energy. ³⁵ Considering the required energy for excitation of ${}^{3}O_{2}$ to ${}^{1}O_{2}$ (0.98 eV) and the first van Hove transitions E_{11} (0.77-1.55 eV) of the direct band gap semiconducting carbon nantobes, ³⁶ the lowest triplet state energies in nanotubes are expected to be high enough to excite oxygen molecules from the ground state to the singlet state. Therefore, our direct observation of ¹O₂ luminescence is also supported thermodynamically. In other recent developments, energy transfer from photoexcited porphyrin molecules to SWNTs³⁷ and the quenching of ¹O₂ by carbon nanotubes via cycloaddition mechanism³⁸⁻⁴² or physical reactions⁴³ have been demonstrated. A lower energy barrier for chemisorbed ${}^{1}O_{2}$ than for ${}^{3}O_{2}$ on nanotube surface 21,44,45 and diameter-dependent band gap in carbon nanotubes^{46,47} were also suggested based on theoretical calculations. In turn, all these events may cause a decrease in ¹O₂ signals, which has been used for the selective control of ¹O₂ formation. ^{43,48} Currently, the knowledge of nanotube based quenching mechanisms as well as subsequent products is limited. Clearly this is an area of research that requires further investigations.

Quantum yield of ${}^{1}O_{2}(\Phi_{\Lambda})$ is an important measure of the photosensitization efficiency. It is usually determined either on a relative basis that requires a reference sensitizer or in an absolute manner using a ${}^{1}O_{2}$ trap. The determination of Φ_{Δ} from SWNT at 532 nm is not precise due to the lack of two-photon reference sensitizer and light scattering by suspended nanoparticles, e.g., ca. 10% reflectance from solid SWNTs at 532 nm. ⁴⁹ Moreover, for an accurate estimation of two-photon Φ_{Λ} , ${}^{1}O_{2}$ intensity, illumination power and two-photon absorption cross section at a given wavelength should be included in Φ_{Λ} calculation. The use of an absolute method would be able to surmount these obstacles, which is an ongoing project in our group. We herein proximate relative Φ_{Δ} by comparing ${}^{1}O_{2}$ intensity from SWNT to that from a reference sensitizer (see supporting information). A well developed sensitizer meso-tetrakis(4sulfonatophenyl)porphyrin (TSPP) with known Φ_{Λ} (0.63 in D₂O) was selected as a reference. ⁵⁰ The ¹O₂ signal was temporally displaced relative to the signals derived from other rapid events synchronized with the laser pulse (i.e., scattered light and fluorescence). Thus, the initial intensity of ¹O₂ was corrected for background interferences using a nitrogen-saturated sample as a control. Our Φ_{Λ} data at 532 nm excitation indicated that ${}^{1}O_{2}$ production was highly dependent upon surface functionalization (figure 2), which is consistent with DMA photooxidation results above. The Φ_{Δ} decreased with the degree of functionalization. For example, the Φ_{Δ} were 0.00, 0.07-0.13 and 0.24-0.53 for samples 1-2, 3-4 and 5-8, respectively.

 $^{1}\text{O}_{2}$ photosensitization is mainly based on the transfer of triplet energy from an excited sensitizer to $^{3}\text{O}_{2}$. Our results imply that the formation of excited triplet states is more efficient in a carbon conjugated surface than in a -COOH functionalized surface. Phenomena with somewhat similar effect was observed by Foote's group for C_{60} and its derivatives. They systematically studied the relationship between fullerene structure and Φ_{Δ} by analyzing a

complete homologous series of fullerene adducts, and found that Φ_Δ decreased as the surface area of the conjugated fullerene core decreased. An obvious reduction in Φ_Δ , 30-40% for CHIT modified and 20-40% for iron catalyst-contained SWNTs was also observed, which may be attributed to the quenching of excited states and 1O_2 , or SWNT surface coverage, by those compounds. Detailed mechanisms require further investigation.

It has been noted that ¹O₂ can be produced upon nonlinear two-photon excitation of a sensitizer. 6,7 In this case the transition proceeds via a virtual state and follows selection rules that can differ from those for a one-photon transition. 8 The spectroscopy based on two-photon excitation has been used for the measurement of exciton binding energies, band-gap energies, ¹¹ and fluorescence emission in SWNTs. ¹² ¹O₂ emission via linear excitation at 266 nm was also reported from a solid sample containing both of silica and SWNTs.⁹ In order to explore the nature of UV and visible photoexcitation in carbon nanotubes, ¹O₂ emission at 1270 nm was monitored as a function of pulsed laser intensity at both 532 and 355 nm. In a one-photon absorption scheme, ¹O₂ intensity should increase linearly with an increase in the intensity of excitation laser. This was indeed the case for SWNTs at excitation wavelength of 355 nm, where the carbon nanotubes had relative strong absorbance (see supporting information.). For two-photon absorption, the ¹O₂ signal is known to be proportional to the square of laser intensity. Upon irradiation of SWNTs at 532 nm, where SWNTs do not have a resonant onephoton transition, the data indeed showed this trend. Figure 3 shows the double logarithmic plot of ¹O₂ intensity against laser intensity at 532 and 355 nm excitation. The nonfunctionalized sample 6 was used for these measurements in order to obtain the better signals. Values of ¹O₂ intensity were calculated by first order kinetic fitting to ¹O₂ decay signals, and laser intensities by an energy meter. Figure 3 indicates that the ¹O₂ data recorded upon 532 nm irradiation in a focused laser beam were not consistent with a one-photon absorption scheme. The linear least squares analysis generated slopes of 2.04±0.11 for 532 nm and 0.99 ±0.03 for 355 nm excitation, which were in line with expected two- and one-photon absorptions.

In conclusion, we herein report the first direct observation of $^1\mathrm{O}_2$ production upon nonlinear excitation of SWNTs, and demonstrate that $^1\mathrm{O}_2$ formation is influenced by several factors including surface functionalization/modification and the existence of residual iron catalyst. $^1\mathrm{O}_2$ emission signals observed upon SWNT irradiation at 532 nm was via a two-photon process, while that at 355 nm was from a one-photon process. The relative Φ_Δ at 532 nm were measured to be 0.00, 0.07-0.13 and 0.24-0.54 for highly-functionalized (samples 1-2), partially-functionalized (samples 3-4) and non-functionalized (samples 5-8) naotubes respectively. The effect of CHIT and iron catalyst on $^1\mathrm{O}_2$ production requires further study. The nanotube-mediated generation of $^1\mathrm{O}_2$ may have applications in both targeted destruction of tumor cells and selective degradation of drug molecules. Our research provides a practical approach to modulate the production of ROS from SWNTs via surface functionalization/ modifications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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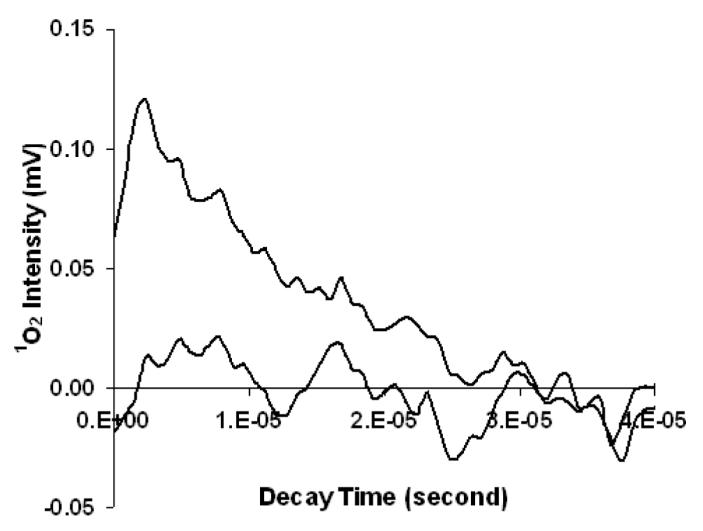


Figure 1. A typical time-resolved $^1\mathrm{O}_2$ emission signal at 1270 nm recorded upon 532 nm irradiation of 15.0 mg/L of air-saturated sample 6 in the absence of (top line) and in the presence of (bottom line) 15 mM NaN3. The decay traces have been corrected for the interference from other rapid events synchronized with the laser pulse (i.e., scattered light and fluorescence), using a same but N2-saturated sample as a control.

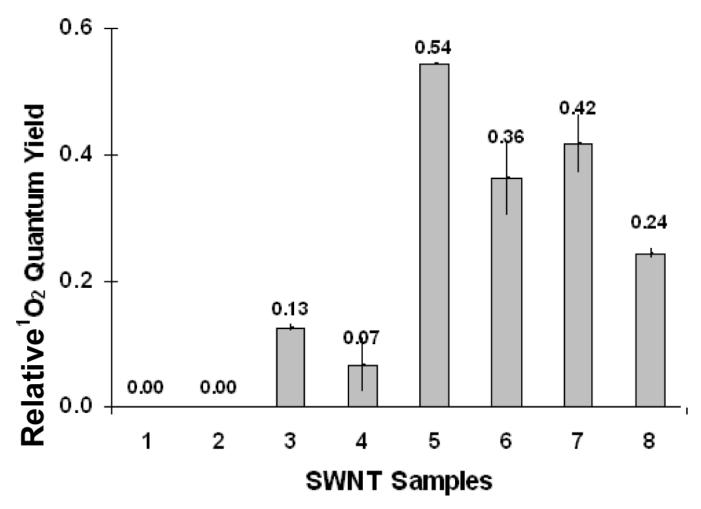


Figure 2. Relative Quantum Yields of ${}^{1}O_{2}$ from SWNTs at 532 nm excitation

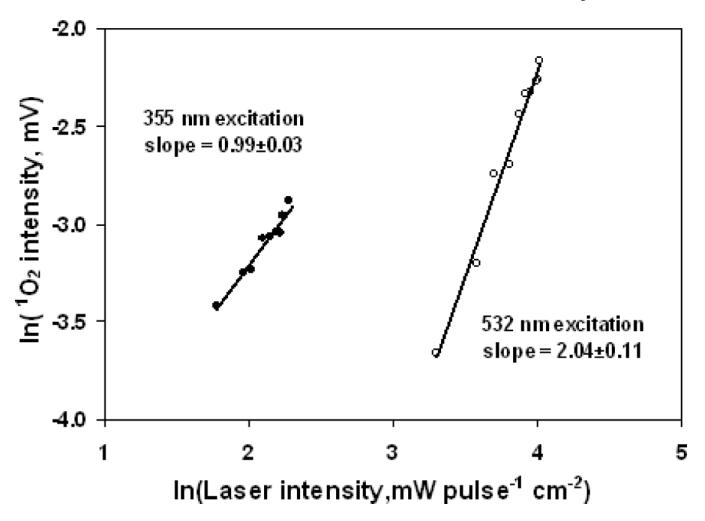


Figure 3. Double logarithmic plot of ${}^{1}O_{2}$ intensity against laser intensity on sample 6 at 355 and 532 nm excitation. Dots and cycles are experimental data and the solid lines are linear least squares fit. The decay traces have been corrected for the interference from other rapid events synchronized with the laser pulse (i.e., scattered light and fluorescence) using a same but N_{2} -saturated sample as a control.

Table 1

SWNT samples used in this work

Sample number	Sample Description		
1	Water dispersible, highly functionalized SWNT in 1:1 D_2O/H_2O (iron-free)		
2	Sample 1 wrapped with CHIT in 1:1 D_2O/H_2O (iron-free)		
3	Water dispersible, partially functionalized SWNT in 1:1 $\mathrm{D}_2\mathrm{O/H}_2\mathrm{O}$ (iron-free)		
4	Sample 3 wrapped with CHIT in 1:1 D ₂ O/H ₂ O (iron-free)		
5	Iron-free, unfunctionalized SWNT in 10% PDDA		
6	Sample 5 wrapped with CHIT in 1:1 D_2O/H_2O (iron-free)		
7	Partially purified SWNT in 10% PDDA (iron concentration of 2 ppm)		
8	Sample 7 wrapped with CHIT in D ₂ O/H ₂ O, 2 ppm iron		

 $\label{eq:Table 2} \mbox{DMA steady-state photooxidation upon 10 min visible illumination of a mixture of 0.5 μg SWNTs and 7.0 $\mu mol DMA in O_2$-saturated DMSO solutions}$

SWNT sample No.	3	5	7
DMA conversion yield (%)	3.6±0.9	9.2±0.7	3.9±0.8