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Helicity-Selective Photoreaction of Single-Walled Carbon Nanotubes with Organosulfur Compounds in the Presence of Oxygen

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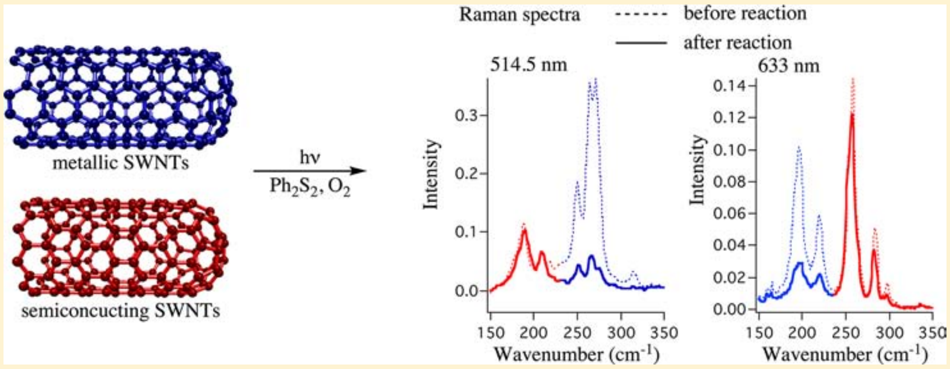
Ⓢ *Supporting Information*



ABSTRACT: This report describes a helicity-selective photoreaction of single-walled carbon nanotubes (SWNTs) with disulfide in the presence of oxygen. The SWNTs were characterized using absorption, photoluminescence (PL), Raman, and X-ray photoelectron spectroscopy, scanning electron microscopy, and current−voltage (*I*−*V*) measurements. Results showed remarkable helicity-selective (metallic SWNTs/semiconducting SWNTs and diameter) functionalization of SWNTs. The reaction rate decreases in the order of metallic SWNTs > semiconducting SWNTs and small-diameter SWNTs > large-diameter SWNTs. Control experiments conducted under various experimental conditions and ESR and femtosecond laser flash photolysis measurements revealed that the helicity-selective reaction proceeds via a photoinduced electron transfer reaction. The PL and *I*−*V* measurements showed that the photoreaction is effective not only to control SWNT conductivity but also for the band gap modulation of semiconducting SWNTs.

■ INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have excellent mechanical and electrical properties that have led to the proposal of many potential applications.[1−4] However, an important obstacle hindering their application is that SWNTs are typically grown as bundles of a mixture of metallic SWNTs (m-SWNTs) and semiconducting SWNTs (s-SWNTs). Selective synthesis of m-SWNTs or s-SWNTs according to their electronic structures persists as an important chal-

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lenge.[5−12] Therefore, practical use of SWNTs requires exfoliation of SWNT bundles and separation of m-SWNTs and s-SWNTs. Chemical functionalization of SWNTs enables their increased dispersibility, exfoliation of their bundle structure, tuning of their electronic properties, integration of SWNTs, construction of a redox system based on SWNTs, and so on.[13,14] Strano et al. reported an interesting selective reaction of SWNTs with 4-chlorobenzenediazonium tetrafluoroborate in which covalent chemical functionalization is controlled by differences in the SWNT electronic structures.[15] The selective reaction of SWNTs with diazonium compounds enables m-SWNTs and s-SWNTs to be enriched.[16,17]

Functionalization of SWNTs with organosulfur compounds has received a great deal of attention. The introduction of thiol groups, which show good affinity with gold, to SWNTs enables effective and site-selective deposition of gold on the SWNTs.[18−21] Dai et al. reported that SWNTs having disulfide bonds played a role as transporters and released functional groups in cells because disulfide bonds are cleaved by enzymes.[22] The organosulfur compounds also act as reactants for functionalization of SWNTs. The C−S bond formation on SWNTs' sidewall was achieved by the addition of thiyl radical and disulfide radical anion.[23,24] A theoretical study revealed that s-SWNTs can be turned to m-SWNTs, which maintain their electronic properties after addition of sulfur, and that thioepoxidation of SWNTs can be used to obtain SWNTs with specific electronic properties.[25] This report describes helicity-selective photoreaction of SWNTs with disulfide in the presence of oxygen.

■ EXPERIMENTAL SECTION

HiPco SWNTs were purchased from Carbon Nanotechnologies Inc. (6,5)-Enriched SWNTs ((6,5) chirality ≥77%; SG 65, designated hereinafter as 65-SWNTs) were purchased from Sigma-Aldrich. Optical absorption spectra were recorded through a Pyrex cell with 10 mm path length using a spectrophotometer (UV-3150; Shimadzu Corp.). Raman spectra were measured using a spectrophotometer (LabRAM HR-800; Horiba Ltd./Jobin-Yvon T64000; Horiba Ltd.) under excitation at 514.5, 633, or 785 nm. The spectra showing the RBM, D-band, and G-band are normalized to the G-band. A tungsten halogen lamp (JCV100 V-500W; Ushio Inc.) was used as a light source. An X-ray photoelectron spectrometer (AXIS-NOVA; Kratos Analytical Ltd.) operated at 15 kV and 20 mA with an Al Kα X-ray source. Current−voltage characteristics of SWNT films were measured using a semiconductor parameter analyzer (4155c; Agilent Technologies Inc.) under ca. 5×10^{-3} Pa. Photoluminescence spectra were measured using the spectrophotometer (NIR-PL system; Shimadzu Corp.). The excitation wavelength was varied from 500 to 800 nm in 10 nm steps, whereas the emission wavelength was varied from 900 to 1300 nm in 1 nm steps. The excitation spectra and the emission slit widths were 10 nm. Scanning electron microscope (SEM) observations were conducted using a field-emission electron microscope (15 kV accelerating voltage, 20 mA beam current, S4500; Hitachi Ltd.). GC/MS spectra were recorded using a gas chromatograph mass spectrometer (GCMS-QP2010 SE; Shimadzu Corp.).

Typical Procedure. First, 0.5 mg of SWNTs was added to 10 mL of a THF solution containing 0.05 M diphenyl disulfide (Ph_2S_2) in a Pyrex glass reactor. The mixture was degassed by three freeze−pump−thaw cycles, purged with oxygen or Ar, and irradiated with a 500 W tungsten halogen lamp. Y-50 (<500 nm; HOYA Corp.) and 3-71 (<470 nm; Daiken Sekiei Glass Corp.) glass filters were used as the cutoff filter.

SWNT thin films were prepared by spraying the SWNT dispersions onto quartz glass using an airbrush. The SWNT dispersion was prepared as follows: 0.4 mg of SWNTs was added to 40 mL of a THF solution containing 0.05 M propylamine. Then the mixture was sonicated for 2 h at 5−10 °C with subsequent centrifugation (14 000*g*, 30 min). During airbrushing, the substrates were heated on a hot plate (ca. 85−100 °C) to evaporate the THF and propylamine. Then, the SWNT thin films on the substrate were washed with methanol to remove the residual amine. The electrical properties of the SWNT film were studied by thermally evaporating gold electrodes onto the film. The length of each electrode was 1 mm. Each was separated by 20 μm.

Typical Procedures for the Preparation of the 65-SWNT Dispersion Using Sodium Dodecylbenzenesulfonate (SDBS) in D_2O. 65-SWNTs or 65-SWNTs treated in a THF solution containing diphenyl disulfide under photoirradiation were added to D_2O containing 1 wt % of SDBS and sonicated for 6 h with a bath-type sonicator. The supernatant solution was used for photoluminescence measurement after centrifugation (45 620*g*, 60 min).

ESR Measurements. A quartz ESR tube (internal diameter: 4.5 mm) containing a deaerated THF solution of SWNTs and diphenyl disulfide was irradiated in the cavity of the ESR spectrometer with focused light of a 1000 W high-pressure Hg lamp (USH1005D; Ushio) through an aqueous filter at low temperature. The ESR spectra were measured at 100 K after photoirradiation under nonsaturating microwave power conditions using a spectrometer (X-band, JES-RE1XE; JEOL) with an attached variable-temperature apparatus. The magnitude of modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra when the maximum slope line width (ΔH_{msl}) of the ESR signals was unchanged with a larger modulation magnitude. The *g* values were calibrated with a Mn^{2+} marker.

Femtosecond Laser Flash Photolysis. Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source (Integra-C, Quantronix), an optical parametric amplifier (TOPAS, Light Conversion Ltd.), and a commercially available optical detection system (Helios; Ultrafast Systems LLC). The sources for the pump and probe pulses were derived from the fundamental output of Integra-C (780 nm, 2 mJ/pulse and fwhm = 130 fs) at a repetition rate of 1 kHz. In our experiments, a wavelength at 480 nm of TOPAS output, which is the fourth harmonic of signal or idler pulses, was chosen as the pump beam. Typically, 5000 excitation pulses were averaged for 5 s to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from time-resolved spectral data. All measurements were conducted at room temperature (295 K).

Computational Details. Geometry optimization and electronic property calculations were performed using the CASTEP package.[26] The plane-wave cutoff energy is 240 eV. A 1 × 1 × 2 *k*-point mesh is used for the Brillouin zone sampling. The convergence tolerance of the maximum force is 0.01 eV/Å. The adsorption energy of molecules on a SWNT is calculated as $E_{ad} = E(\text{SWNT}) + E(\text{molecule}) - E(\text{SWNT + molecule})$.

■ RESULTS AND DISCUSSION

A THF solution of SWNTs containing diphenyl disulfide was sonicated in a bath-type sonicator for 2 h. The dispersion was irradiated under ambient conditions with a 500 W halogen lamp. Figure 1 shows the visible−near-infrared (vis−NIR) spectra of SWNTs in THF before and after the reaction. Three typical absorption bands are observed at approximately 1600−1000, 1000−600, and 600−400 nm.[27] The first two bands are attributed to electronic transitions of the first (S_{11}) and second (S_{22}) van Hove singularities in s-SWNTs. The third band is attributed to that of the first singularities in m-SWNTs (M_{11}). After irradiation, absorption peaks of m-SWNTs significantly decreased though the peaks of s-SWNTs having small diameters slightly decreased. The characteristic feature of s-SWNTs remained even when the characteristic feature of m-SWNTs disappeared. This indicates that a helicity-selective reaction occurs.

Raman spectroscopy is a powerful method to obtain evidence of covalent sidewall functionalization.[28] Pristine SWNTs exhibit

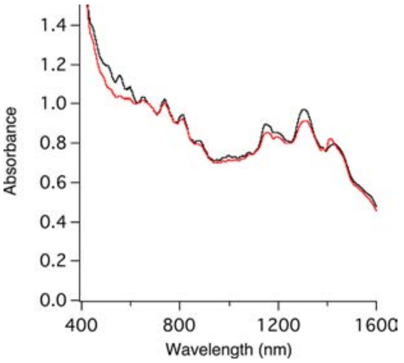


Figure 1. Absorption spectra of SWNTs after photoreaction (>300 nm) in a THF solution containing 0.05 M Ph_2S_2 under ambient condition: black, 0 h; red, 14 h.

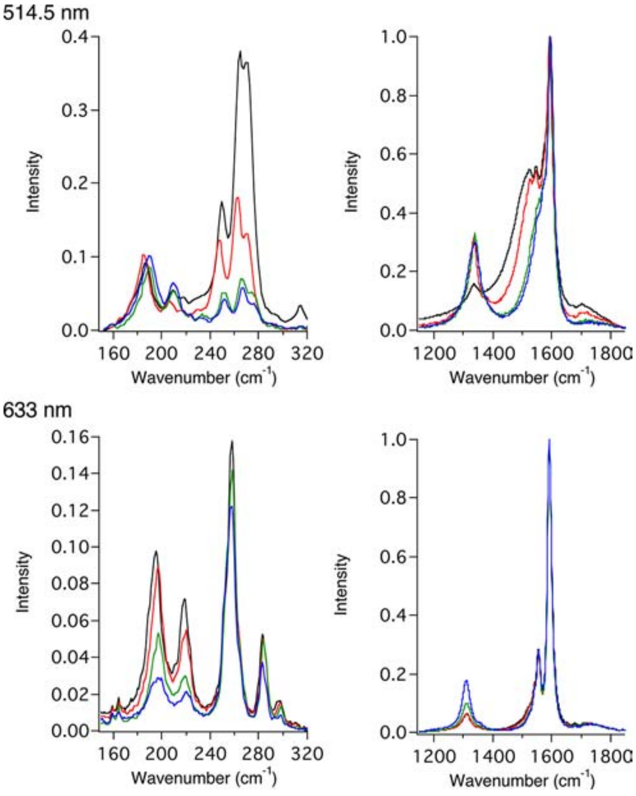


Figure 2. Raman spectra of SWNTs after photoreaction (>300 nm) in a THF solution containing 0.05 M Ph_2S_2 under ambient conditions: black, 0 h; red, 0.5 h; green, 3 h; blue, 6 h.

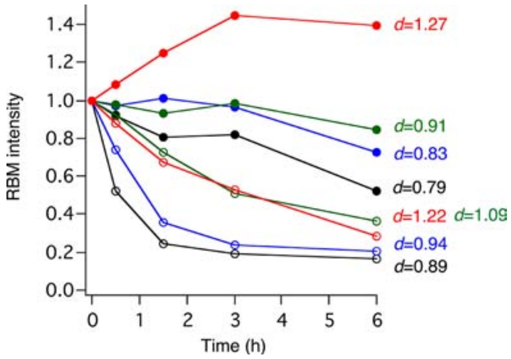
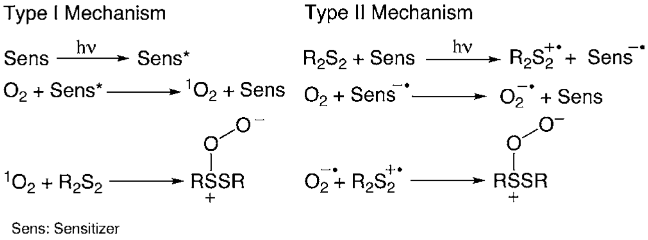
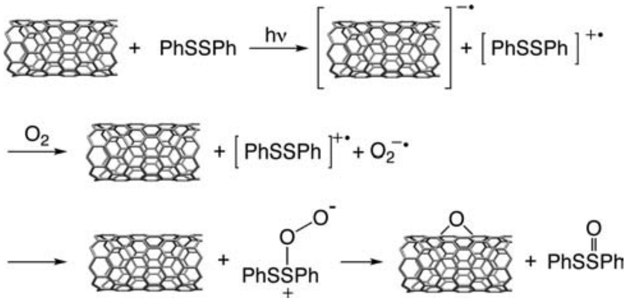


Figure 3. Changes of RBM intensity (Int/Int_{0h}) of SWNTs during photoreaction (>300 nm) in a THF solution containing 0.05 M Ph_2S_2 under ambient conditions: open circle, m-SWNTs; solid circle, s-SWNTs.

Scheme 1



Scheme 2



two strong bands: the radial breathing mode (RBM) at 160−300 cm^{-1} and the G-band at around 1590 cm^{-1}. The weak band around 1300 cm^{-1}, the disorder mode (D-band), is attributed to sp^3-carbon in the hexagonal framework of the SWNT walls. The increased D/G ratio observed after the reaction suggested that sidewall functionalization of SWNTs occurred.[29,30] The RBM peaks appear around 260 and 200 cm^{-1} when m-SWNTs are excited at 514.5 and 633 nm, respectively, whereas peaks appear around 180 and 260 cm^{-1} when s-SWNTs are excited, respectively, at 514.5 and 633 nm.[31] During irradiation, the characteristic RBM peaks assigned to m-SWNTs were decreased selectively with a decrease of Breit−Wigner−Fano line shape peaks (Figure 2 and Supporting Information Figure S1). The result agrees with the absorption spectra, which indicates the selective functionalization of m-SWNTs in the photoreaction.[32]

The SWNT diameters were estimated as 1.27, 0.94, 0.89, and 0.87 nm (514.5 nm) and 1.22, 1.09, 0.91, 0.83, and 0.79 nm (633 nm) from the equation $\omega_{RBM} = Ad_t^{-1} + B$ (A = 223.5 cm^{-1} and B = 12.5 cm^{-1}), where ω_{RBM} is the wavenumber of RBM.[33,34] We found that the reaction depends on not only the electronic properties of SWNTs but also its diameter. The plot of the decrease of each RBM intensity against reaction time shows that the large-diameter SWNTs are less reactive than the small-diameter SWNTs (Figure 3). From the Raman and absorption spectra, the order of the photoreactivity of SWNTs is m-SWNTs > s-SWNTs and small-diameter SWNTs > large-diameter SWNTs.

To clarify the reaction details, the photoreaction of SWNTs with diphenyl disulfide was conducted under various conditions. The photoreaction was suppressed in the absence of oxygen or diphenyl disulfide (Figure S3). By contrast, the photoreaction was accelerated under saturated oxygen. The reaction did not proceed without light irradiation, whereas the photoreaction proceeded even if we cut off the light in the disulfide absorption wavelength region (shorter than 420 nm).

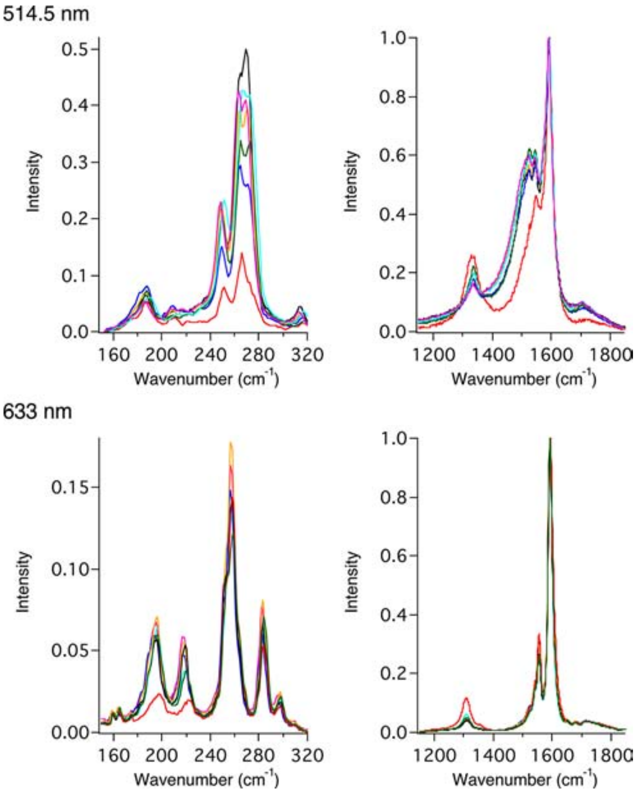


Figure 4. Raman spectra of SWNTs before (black) and after photoreaction (>470 nm) in a THF solution containing 0.05 M Ph_2S_2 under saturated oxygen in the presence of scavenger (0.05 M): red, none; aqua, DABCO; green, methanol; pink, BHT; orange, TEMPO; blue, $(^n\mathrm{BuO})_3P$.

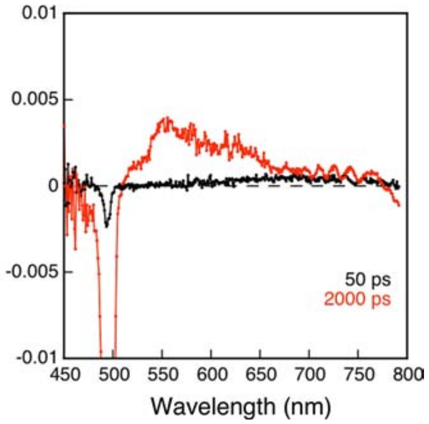


Figure 5. Transient absorption spectra of SWNTs with Ph_2S_2 (1.0 M) in THF taken at 50 and 2000 ps after femtosecond laser excitation at 480 nm.

Therefore, we concluded that photoexcited SWNTs are the key component to produce the reaction.

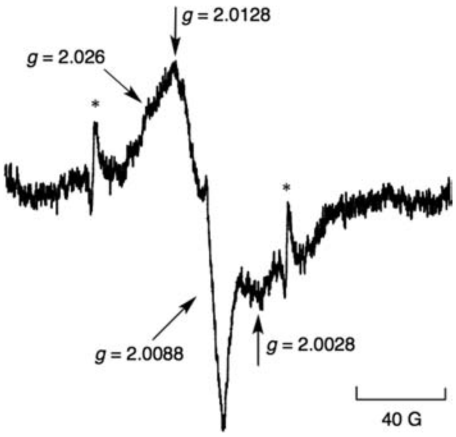


Figure 6. ESR spectrum of an O_2-saturated THF solution containing Ph_2S_2 and SWNTs after photoirradiation by a high-pressure Hg lamp at 100 K. Asterisks denote Mn^{2+} markers.

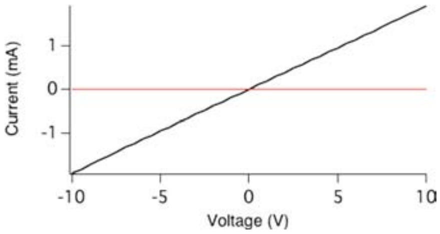


Figure 7. Current versus voltage characteristics of SWNT films before (black) and after (red) photoreaction of SWNTs with Ph_2S_2 in the presence of oxygen.

Reportedly, the photoreaction of sulfide and disulfide under oxygen in the presence of a photosensitizer affords persulfoxide and thiopersulfinate intermediates, which act as nucleophilic oxidizing agents.[35] For example, C_{60} is transformed to fullerene epoxides in the reaction with persulfoxide intermediate, which was generated by the reaction of singlet oxygen ($^1O_2$) and sulfide.[36] In this context, we inferred that photogenerated thiopersulfinate is the key intermediate for the reaction. Two mechanisms have been suggested for the generation of thiopersulfinate.[35,37] In the type I mechanism, $^1O_2$ which is generated by the energy transfer from excited sensitizer reacts with disulfide to produce the related thiopersulfinate. On the other hand, in the type II mechanism, disulfide radical cation and sensitizer radical anion are initially produced by the photoirradiation. Then, sensitizer radical anion transfers an electron to O_2 to produce $O_2^{-\bullet}$, which reacts with the disulfide radical cation to produce the respective thiopersulfinate (Scheme 1). First, we tried to figure out in which mechanism the present reaction proceeded. Murray et al. reported that the diphenyl disulfide shows lower reactivity toward $^1O_2$ than both diethyl sulfide and diethyl disulfide.[37] To clarify the reaction intermediate, photoreaction of SWNTs with diethyl sulfide or diethyl disulfide was conducted. As shown in Figure S4, photoreaction of SWNTs was suppressed when diethyl sulfide or diethyl disulfide was used instead of diphenyl disulfide. From these experimentally obtained results, the type I mechanism, involving generation of $^1O_2$, is excluded from this reaction. In other words, the type II mechanism involving the electron transfer mainly contributed to this reaction.

From these experimentally obtained results, we speculated the reaction mechanism as shown in Scheme 2. The generated SWNT radical anion transfers an electron to oxygen forming $O_2^{-\bullet}$.[38,39] Recombination of the disulfide radical cation and $O_2^{-\bullet}$ produces the thiopersulfinate intermediate. The proposed mechanism was supported by the following controlled experiments (Figure 4). Addition of 1,4-diazabicyclo[2.2.2]-octane (DABCO), tributyl phosphite ($(^n\mathrm{BuO})_3P$), methanol, butylhydroxytoluene (BHT), and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) suppressed the photoreaction. DABCO and TEMPO act as an electron transfer quencher, methanol and

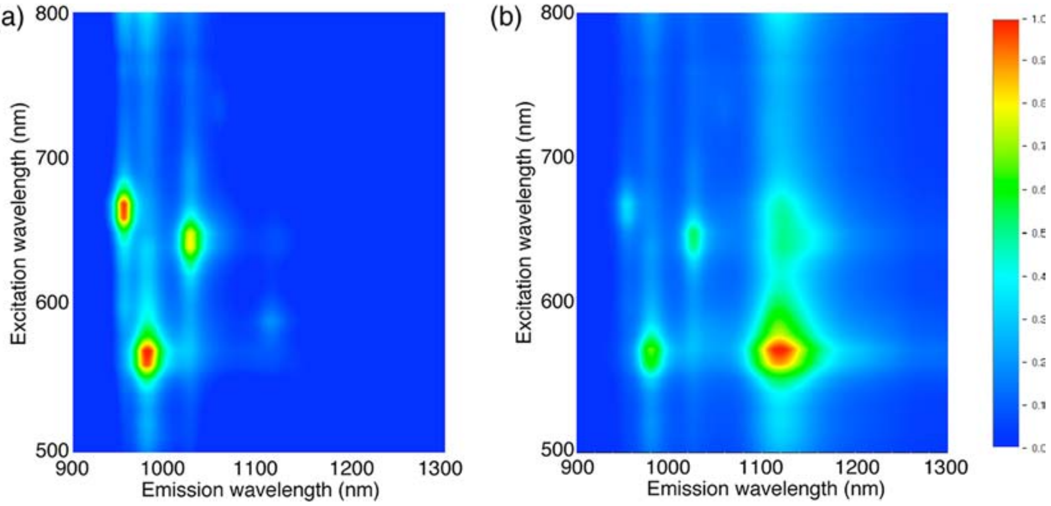


Figure 8. Contour plots of fluorescence intensity versus excitation and emission wavelengths for 65-SWNTs suspended in D_2O containing SDBS: (a) pristine sample; (b) photoirradiated for 12 h in a THF solution containing 0.05 M Ph_2S_2. See Figure S9 for the absorption and Raman spectra of the SWNTs.

Table 1. Adsorption Energy E_{ad} (eV) and Mulliken Charge Transfer Q ($|e|$) for Ph_2S_2 Adsorption on the (13,0) and (7,7) SWNTs

	(13,0)		(7,7)	
compound	E_{ad}	Q	E_{ad}	Q
PhSSPh	0.50	0.05	0.54	0.04

$(^n\text{BuO})_3\text{P}$ act as a nucleophilic oxygen atom scavenger, and BHT and TEMPO act as radical scavengers.[40−47] Formation of thianthrene[48,49] and 1,4-bis(phenylthio)benzene[50,51] from diphenyl disulfide radical cation was reported. Not only *S*-phenyl benzenesulfonothioate[35] but also thianthrene and 1,4-bis(phenylthio)benzene were detected by GC−MS analysis of the filtrate of the reaction mixture of SWNTs with diphenyl disulfide (Figure S5).

To obtain evidence of the radical mechanism, femtosecond laser flash photolysis transient absorption measurements were conducted in a THF solution containing SWNTs and diphenyl disulfide. A transient absorption band at 550 nm observed at 2 ns after femtosecond laser excitation at 480 nm is assigned to the thianthrene radical cation formed from rearrangement of diphenyl disulfide radical cation (Figure 5).[52] The radical species were also detected using ESR measurements conducted under photoirradiation in an O_2-saturated frozen THF glass at 100 K. As shown in Figure 6, an anisotropic ESR signal was observed at $g_1 = 2.0128$, $g_2 = 2.0088$, and $g_3 = 2.0028$ ($g_{av} = 2.0081$), which is assigned to the thianthrene radical cation formed from rearrangement of the diphenyl disulfide radical cation.[48,53] The diphenyl disulfide radical cation was also observed as a shoulder peak at $g = 2.026$. This result constitutes proof of the electron transfer mechanism.

The present selective reaction system also has an advantage in their simplicity. Generally, the dispersibility and degree of exfoliation of SWNTs are important for chemical functionalization, especially the helicity-selective reaction. For example, the selective reaction of SWNTs with diazonium compound was conducted using exfoliated SWNTs prepared in aqueous solution containing surfactant by sonication and centrifugation.[15−17] By contrast, the helicity-selective reaction of SWNTs with diphenyl disulfide proceeded without pretreatment and exfoliation of SWNT bundles using surfactant. Reductive alkylation of SWNTs was well investigated, and it was revealed that the SWNT anion species shows high reactivity and SWNT bundles are well exfoliated due to the repulsion of anion charge of the reduced SWNT surface.[39,54] Formation of SWNT anion species via electron transfer, which exfoliates the SWNT bundles, might be an important factor for the present helicity-selective reaction. The SWNT films on the quartz were used in the photoreaction with disulfide in the presence of oxygen. The reaction proceeded only when the film was immersed in a THF solution containing diphenyl disulfide (Figure S6).

The amount of oxygen in the SWNTs after the photoreaction was estimated from results of XPS analysis. The XPS spectra of the SWNTs obtained before and after the photoreaction showed no peak attributable to sulfur, although peaks related to carbon and oxygen were observed around 285 eV (C 1s) and 531 eV (O 1s) (Figure S7). The atomic ratios of C to O ([C]/[O]) in SWNTs were 45.0 and 11.0 before and after the photoreaction. The XPS results indicate that oxygen was introduced on the SWNT surface in the photoreaction, which is consistent with the plausible reaction mechanism, as shown in Scheme 2.

Sheet resistivity measurements of SWNT films were performed before and after the photoreaction. The SWNT conductivity was decreased to about 1/1000 after the photoreaction. The decrease is explainable in terms of the selective functionalization of m-SWNTs (Figure 7). Chemical modification of m-SWNTs destructs π-conjugation, which caused a decrease of the electron conduction. Recently, band gap modulation of s-SWNTs was reported by Ghosh et al.[55] They reported that the photoluminescence spectra of s-SWNTs were red-shifted by the small amount of oxygenation. In this context, photoluminescence experiments of SWNTs treated with diphenyl disulfide were conducted. It is particularly interesting that a red shift of photoluminescence was observed from 980 to 1120 nm for (6,5) SWNT (Figures 8 and S8). Similar red shifts were observed for (7,5) and (8,3) SWNTs. This result indicates that the photoreaction is effective for tuning electronic properties not only of m-SWNTs but also of s-SWNTs.

The selective interaction of SWNTs with diphenyl disulfide in the ground state was studied using the local density functional theory and ultrasoft pseudopotential plane-wave methods. Because the reactivity of SWNTs depends on their diameters (SWNTs having smaller diameters show higher reactivity), the (7,7) and (13,0) tubes having diameters of 1.02 and 0.952 nm were chosen as typical m-SWNTs and s-SWNTs, respectively. Theoretical calculations show no marked differences in the adsorption energies of diphenyl disulfide toward m- and s-SWNTs in the ground state (Table 1). The results excluded the selective exfoliation of m-SWNTs, which might increase their reaction efficiency. The selective reaction of m-SWNTs might originate from the electron-accepting ability of m-SWNTs,[56] which makes their reactivity toward thiopersulfinate higher than that of s-SWNTs.

CONCLUSION

In summary, m-SWNTs were functionalized efficiently and selectively with diphenyl disulfide under mild conditions. The controlled experiments and ESR and LFP experiments suggest that the reaction is induced by electron transfer from excited SWNTs to disulfide. XPS and photoluminescence experiments show that the oxygenation of SWNTs proceeded, and the addition of oxygen atoms effectively controls the electronic properties not only of m-SWNTs but also of s-SWNTs. This selective functionalization is useful for the separation of electronic characteristic SWNTs. Diameter selectivity observed in this reaction is useful for the sorting of SWNTs when the SWNTs have similar electronic types.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Raman spectra, absorption spectra, XPS spectra, fluorescence spectra, SEM images, and MS spectra of the reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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