

Changes in the Fluorescence Spectrum of Individual Single-Wall Carbon Nanotubes Induced by Light-Assisted Oxidation with Hydroperoxide

M. Zhang,^{*,†} M. Yudasaka,^{†,‡} Y. Miyauchi,[§] S. Maruyama,[§] and S. Iijima^{†,‡,||}

SORST-JST, c/o NEC, 34 Miyukigaoka, Tsukuba, Ibaraki, 305-8501, Japan, NEC, 34 Miyukigaoka, Tsukuba, Ibaraki, 305-8501, Japan, Tokyo University, Bunkyo-ku, Tokyo 113-8656, Japan, and Meijo University, Tempaku-ku, Nagoya 468-8502, Japan

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Through fluorescence-spectrum measurements, we investigated the effects of light-assisted oxidation with H_2O_2 (LAOx) on single-wall carbon nanotubes (SWNTs) that were individually dispersed in an aqueous solution of surfactant. The intensities of the fluorescence spectra were decreased remarkably by the LAOx when the light's wavelength was 400–500 nm and a little when 600–700 nm. The spectrum intensity did not recover even when the pH was restored to an original value of 6.5. The spectra changed little when the LAOx wavelength was 500–600 nm or the light was not irradiated. In addition, the effect of LAOx on SWNTs was related to the diameters of SWNTs. We inferred that these phenomena reflected that H_2O_2 was dissociated by absorbing the fluorescence light emitted from optically excited SWNTs, which, in turn, accelerated the burning out of SWNTs.

Introduction

Single-wall carbon nanotubes (SWNTs)¹ have attracted the attention of many researchers in various fields because of their interesting properties and potential applications.² The chemistry of SWNTs has been investigated with regard to purification,^{3–12} chemical functionalization,^{7,10,13–15} and the separation of tubes of different types (either metallic or semiconducting).^{16–18} In these processes, the oxidation of SWNTs plays important roles. The purification of as-grown SWNTs involves³ combustion in O_2 gas as well as treatment with strong acids such as HNO_3 ,^{5,6} and $\text{H}_2\text{SO}_4/\text{HNO}_3$.⁷ Strong-acid treatments have also been used to open the tube ends and to cut long ropes of SWNTs into shorter lengths.⁷ The combustion has also been used to narrow the diameter distribution of SWNTs^{19,20} since SWNTs with smaller diameters combust more easily than those with larger diameters.²¹ Recently, a method of light-assisted oxidation with H_2O_2 (LAOx) was proposed for selectively eliminating SWNTs with certain diameters.²² However, it is not easy to understand the underlying phenomena of the LAOx, mainly because SWNTs aggregate and form bundles.

Technical advances in nanotube dispersion²³ now enable us to obtain individual SWNTs in an aqueous solution of surfactants such as sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (NaDDBS),²⁴ or polymaleic acid/octyl vinyl ether (PMAOVE).²⁵ Photoexcitation can cause individual semiconducting SWNTs to exhibit fluorescence in near-IR regions, and from this fluorescence the electronic structures of semiconducting nanotubes have been elucidated.^{23,26}

Through fluorescence-spectrum measurement, we studied the effects of LAOx on individual SWNTs dispersed in an aqueous solution of NaDDBS. Our results confirmed that visible-light

irradiation accelerated the oxidation of SWNTs with H_2O_2 , which is consistent with our previous results obtained using SWNT bundles.²² We also found that the quenching of SWNT fluorescence became irreversible as a result of LAOx, indicating that SWNTs were burnt out. Moreover, we found that the effect of LAOx on SWNTs was related to both the wavelengths of light applied for the LAOx and the diameters of SWNTs.

Experimental Section

The as-grown SWNTs used in this study were HiPco SWNTs²⁷ purchased from Carbon Nanotechnology Incorporated. To remove iron impurities from the SWNTs, we treated the as-grown SWNTs in oxygen at 320 °C for 30 min to take the graphitic shell off the iron particles and then dispersed the SWNTs in 30% HCl at 60 °C for 5 h followed by centrifuging. After decanting the supernatant, we washed the sediment with distilled water by using a centrifuge several times until the pH value was close to 7. The final sediments of SWNTs were dried with a freezing drier and further dried at 200 °C under vacuum (50–100 Torr) for 1 h to remove water molecules and electrolytes trapped inside the SWNTs.²⁸ The initial iron quantity contained in the SWNTs was about 40%, which was reduced to about 5% after the purification. The iron quantity was estimated through thermogravimetric measurements.

The purified HiPco SWNTs were dispersed in D_2O containing 0.5 wt % NaDDBS by using an ultrasonic processor equipped with a titanium alloy tip for 90 min at about 300 W/cm². The obtained dispersions were then centrifuged at 220 000g for 2–3 h, and about 70% of the supernatant volume was collected. It is believed that SWNTs prepared in this way (denoted as SWNT-NaDDBS- D_2O) mainly consist of isolated individual SWNTs.^{23,24} The fluorescence spectrum of SWNT-NaDDBS- D_2O was measured in ranges of the excitation wavelength of 350–800 nm and a fluorescence wavelength of 800–1400 nm using a HORIBA SPEX Fluorelog-3-11 Spectrofluorometer, and the results were exhibited in a contour plot of fluorescence intensity vs excitation and emission wavelengths.

* Corresponding author. E-mail: minfang@frl.cl.nec.co.jp.

[†] SORST-JST.

[‡] NEC.

[§] Tokyo University.

^{||} Meijo University.

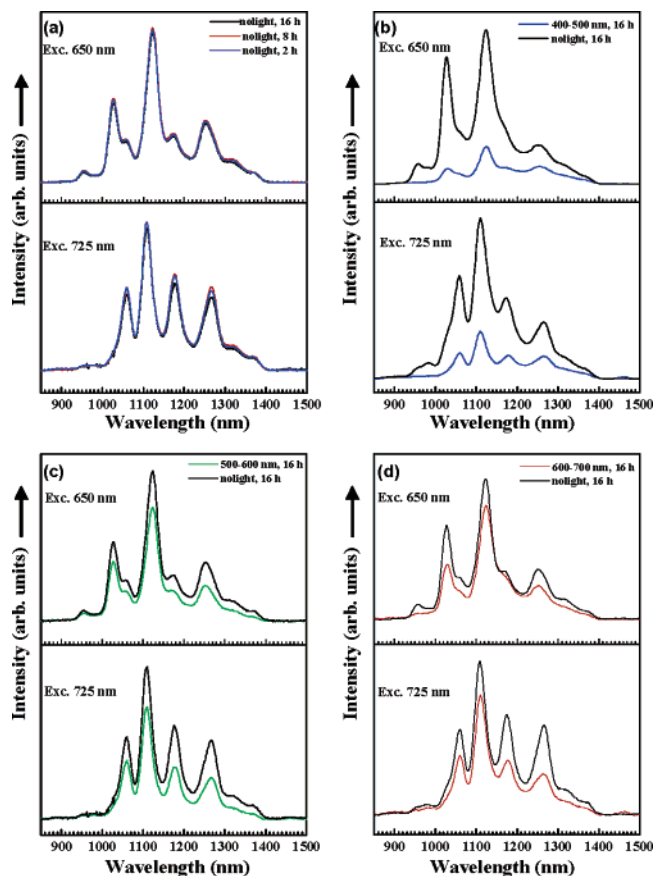


Figure 1. Fluorescence spectra (excitation wavelength, 650 and 725 nm) of SWNT-NaDDBS-H₂O₂ left for various periods in darkness (a) and with light irradiation (LAOx) at wavelength bands of 400–500 (b), 500–600 (c), and 600–700 nm (d). For easy comparison, the black line of part a is added in parts b, c, and d.

LAOx was performed as follows. The SWNT-NaDDBS-D₂O was mixed with 30% H₂O₂ aqueous solution. The volume ratio of the SWNT-NaDDBS-D₂O to the aqueous H₂O₂ solution was 1:1. This mixture is denoted as SWNT-NaDDBS-H₂O₂ hereafter. The optical absorption spectrum of the 30% H₂O₂ aqueous solution and SWNT-NaDDBS-H₂O₂ were measured with Lambda 19 UV/VIS/NIR spectrometer (Perkin-Elmer Corp.). Immediately after the mixing, the LAOx was started on SWNT-NaDDBS-H₂O₂ at different wavelength bands at room temperature for various periods. The wavelength bands were 400–500, 500–600, and 600–700 nm, which were obtained from a xenon lamp equipped with various optical band-pass filters. To eliminate infrared lights, a water filter that was set in front of the SWNT-NaDDBS-H₂O₂ during the LAOx. The light powers of the three light bands at the specimens were about 100 mW/cm².

Soon after LAOx ended, the fluorescence spectra of the SWNT-NaDDBS-H₂O₂ and pH were measured. The excitation wavelength was 650 or 725 nm, which corresponded to the second band gaps (E₂₂) of SWNTs.²⁹ The fluorescence was detected in the range of 800 and 1500 nm, which corresponded to the first band gap (E₁₁) of semiconducting SWNTs.²⁹

Results

The fluorescence spectra of SWNT-NaDDBS-H₂O₂ are shown in Figure 1. Each peak corresponds to the emission from the first band gap (E₁₁) of a semiconducting SWNT. It is clear that the spectrum remained almost unchanged when the SWNT-NaDDBS-H₂O₂ was left without the light irradiation

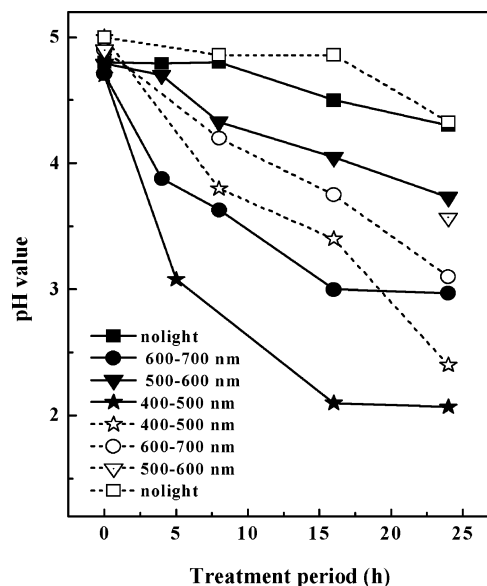


Figure 2. Changes in the pH values of SWNT-NaDDBS-H₂O₂ (solid lines) and NaDDBS-H₂O₂ solutions (broken lines) with an increase of periods left in darkness or LAOx at various wavelength bands of 400–500, 500–600, and 600–700 nm.

at room temperature for about 4–24 h (Figure 1a). However, when the LAOx's with various wavelengths for about 16 h were performed on the SWNT-NaDDBS-H₂O₂, their spectra changed. The LAOx with the light bandwidth of 400–500 nm (Figure 1b) induced a large decrease in the intensity of SWNT emission peaks, while that with 500–600 nm (Figure 1c) or 600–700 nm (Figure 1d) caused smaller decreases.

Figure 2 shows that the pH values of the SWNT-NaDDBS-H₂O₂ and NaDDBS-H₂O₂ (without SWNTs) decreased as the LAOx period became longer. The greatest decrease in the pH of SWNT-NaDDBS-H₂O₂ was observed when the LAOx wavelength was 400–500 nm, followed in order by 600–700 nm, 500–600 nm, and without light irradiation. By comparison of the pH decrease of SWNT-NaDDBS-H₂O₂ with that of NaDDBS-H₂O₂,³⁰ the decrease of pH of SWNT-NaDDBS-H₂O₂ was greater, clearly showing the effect of the LAOx on SWNTs. After LAOx for 24 h, we added several droplets of Ba(OH)₂ aqueous solution to the SWNT-NaDDBS-H₂O₂ and NaDDBS-H₂O₂. We noticed that the transparent solution changed to a white cloudy suspension (not shown), which might have been due to particle generation of water-insoluble BaCO₃ and/or BaSO₄. This indicates that SWNTs and NaDDBS were degraded by H₂O₂ and generated CO₂, CO₃²⁻, and SO₄²⁻.

Since it is reported that the pH of an SWNT solution affects the fluorescence spectra of SWNTs,^{23,31} we also investigated this influence. We changed the pH of SWNT-NaDDBS-H₂O₂ (24 h, no light irradiation) with 0.2 M HCl and 0.2 M NaOH in the order of 6.5 → 4 → 2 → 6.5, and measured the fluorescence spectra at each pH. We found that the peak intensities decreased as the pH fell, and then recovered when the pH returned to 6.5 when no light was irradiated (Figure 3a). However, the spectrum peaks that decreased after LAOx did not recover even when the pH was restored to 6.5. For example, after LAOx at 400–500 nm for 24 h (Figure 3b), the fluorescence intensities of the SWNT-NaDDBS-H₂O₂ greatly decreased (red lines) accompanying the pH decrease from about 6.5 to 2.0. The decreased fluorescence intensities did not recover even when the pH was restored to 6.5 (blue lines).

By adjustment of the pH values to 6.5, the changes of fluorescence spectra of SWNT-NaDDBS-H₂O₂ caused by the

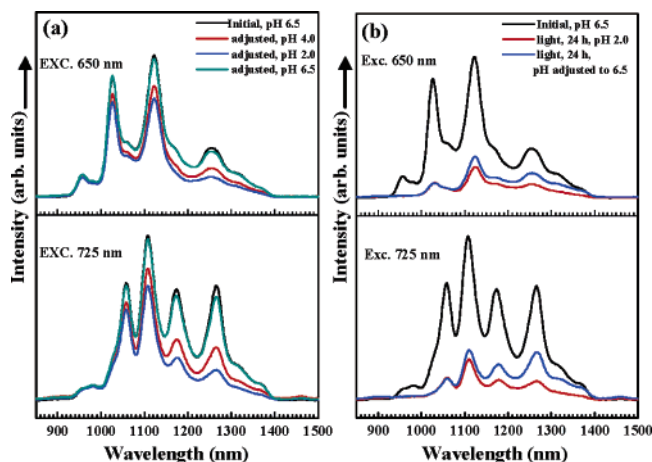


Figure 3. (a) Fluorescence spectra (excitation wavelength, 650 and 725 nm) of SWNT–NaDDBS–H₂O₂ after being left in darkness for 24 h; pH 6.5 (black curve) and that after the pH was adjusted to 2.0, 4.0, and 6.5. (b) Fluorescence spectra of SWNT–NaDDBS–H₂O₂ after LAOx at 400–500 nm for 24 h; pH 2.0 (red curve) and that after the pH was adjusted to 6.5 (blue curve).

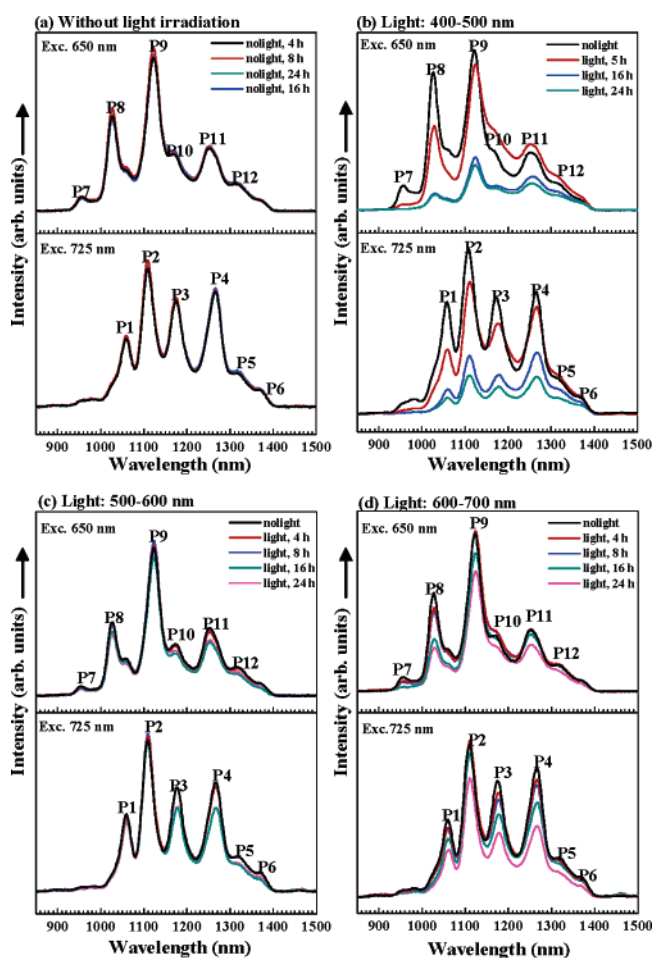


Figure 4. Fluorescence spectra (excitation wavelength, 650 and 725 nm) of the SWNT–NaDDBS–H₂O₂ after being left in darkness (a), and those after LAOx for 4–24 h at 400–500 (b), 500–600 (c), and 600–700 nm (d). The fluorescence spectra were measured after the pH was adjusted to 6.5.

LAOx at 400–500, 500–600, and 600–700 nm for various periods appeared as shown in Figure 4. These fluorescence spectra in Figure 4 were not different very much from those measured without adjusting the pH values at 6.5 (Figure 1). The degree of spectral quenching by the LAOx followed the

TABLE 1: Structures of (n,m) SWNTs Corresponding to the P1–P12 peaks in Figure 4

$-(I - I_0)/I_0$ (%)	400–500 nm (2.48–3.1 eV)		600–700 nm (1.77–2.07 eV)	
	(n,m)	dt (nm)	(n,m)	dt (nm)
> 80%	P7: (6,5)	0.76	P7: (6,5)	0.76
> 60%	P8: (7,5)	0.83		
	P1: (10,2)	0.88		
	P3: (8,6)	0.97		
	P2: (9,4)	0.91		
> 30%	P9: (7,6)	0.89		
	P4: (8,7)	1.03		
	P11: (9,5)	0.96	P8: (7,5)	0.83
	P5: (9,7) ^a	1.10 ^a	P6: (11,4)	1.11
> 10%	P12 ^a		P3: (8,6)	0.97
			P4: (8,7)	1.03
			P1: (10,2)	0.88
			P5: (9,7) ^a	1.10
			P12 ^a	1.10 ^a
			P11: (9,5)	0.96
			P9: (7,6)	0.90
			P10 ^a	0.97 ^a
			P2: (9,4)	0.92

^a The chiral indexes of P10 and P12 could not be assigned according to the study of Weisman et al.³²

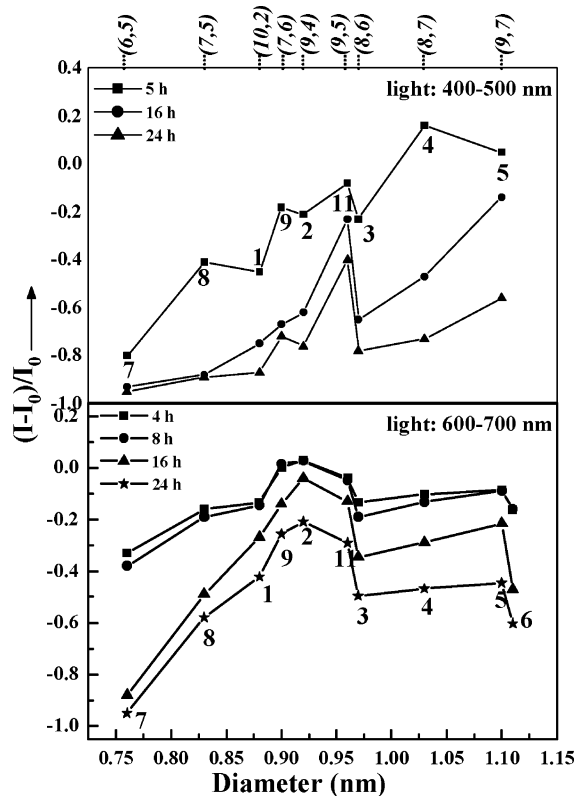


Figure 5. Quenching coefficients, $-(I - I_0)/I_0$, for various periods of LAOx are indicated as a function of the SWNT diameters. Here, “I” and “ I_0 ” refer to the fluorescence-peak heights of the SWNT–NaDDBS–H₂O₂ after LAOx and being left in dark, respectively. These values were calculated from the Lorentzian deconvolution of the fluorescence spectra for SWNT–NaDDBS–H₂O₂ left in darkness and after LAOx at 400–500 and 600–700 nm for various lengths of time (parts b and d of Figure 4).

order 400–500 nm \gg 600–700 nm \gg 500–600 nm > no irradiation of light.

To clarify the influence of LAOx at 400–500 and 600–700 nm on SWNTs, we analyzed the pH-corrected fluorescence spectra of SWNT–NaDDBS–H₂O₂ in parts b and d of Figure 4 by Lorentzian deconvolution. The spectra in parts b and d of

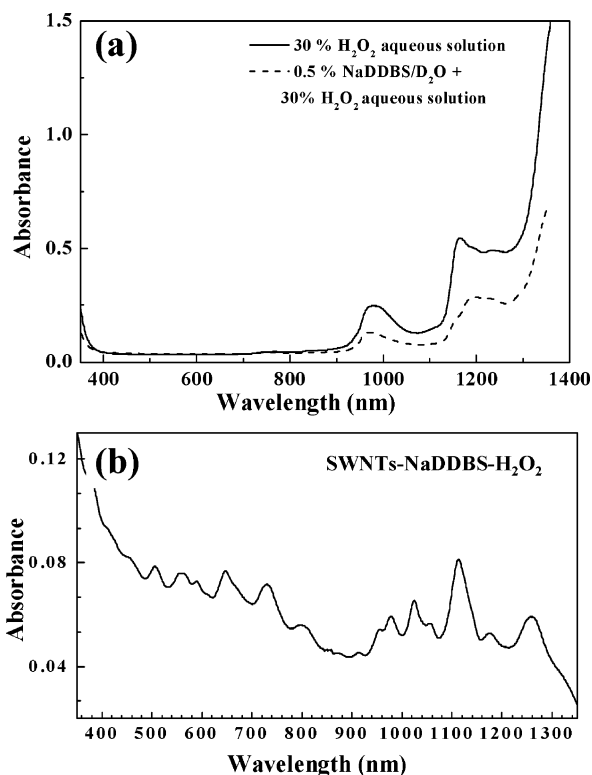


Figure 6. Absorption spectra of (a) 30% aqueous solution of H_2O_2 and NaDDBS- H_2O_2 and (b) SWNT-NaDDBS- H_2O_2 .

Figure 4 were deconvoluted into 12 peaks (P1–P12). The chiral indexes of SWNTs corresponding to P1–P12 were assigned according to the empirical Kataura plots.³² In Table 1, chiral indexes are listed in the order of the fluorescence quenching coefficient. The quenching coefficient is defined as $-(I - I_0)/I_0$ where I_0 and I refer to the emission-peak heights of the SWNT-NaDDBS- H_2O_2 before and after LAOx, respectively. The quenching coefficients, $-(I - I_0)/I_0$, for P1–P12 are plotted against the SWNT diameters in Figure 5 for various periods of LAOx. The graphs in Figure 5 for 400–500 nm irradiation (top) and 600–700 nm irradiation (bottom) show that the fluorescence quenching was largest for small-diameter (<0.9 nm) SWNTs. It is curious that the quenching for large diameter (>0.97 nm) SWNTs exceeded that for SWNTs with moderate diameters (0.9–0.97 nm).

Discussion

Our results indicated that light irradiation of the SWNT-NaDDBS- H_2O_2 enhanced the decrease in the solution's pH (Figure 2) and the fluorescence quenching of SWNTs (Figure 1). The decreased intensities did not recover even after the pH values were restored to the initial pH of 6.5 (Figures 3 and 4). This differed from the findings of Dukovic et al.,²⁵ Strano et al.,³¹ and Zhao et al.³³ These three studies indicate that the optical-absorption bleaching and luminescence quenching are caused by the formation of nanotube oxides or functional groups on the SWNT surface at low pH, and this can be completely reversed by adjusting the pH. We believe that the irreversibility of the fluorescence spectra in our experiments indicates that the SWNTs were burnt out as a result of LAOx. This also could be proved by our previous study²² and the changes of the fluorescence spectra of SWNTs caused by the LAOx without surfactant, which is shown as the contour plot of the excitation-fluorescence spectra (Supporting Information).

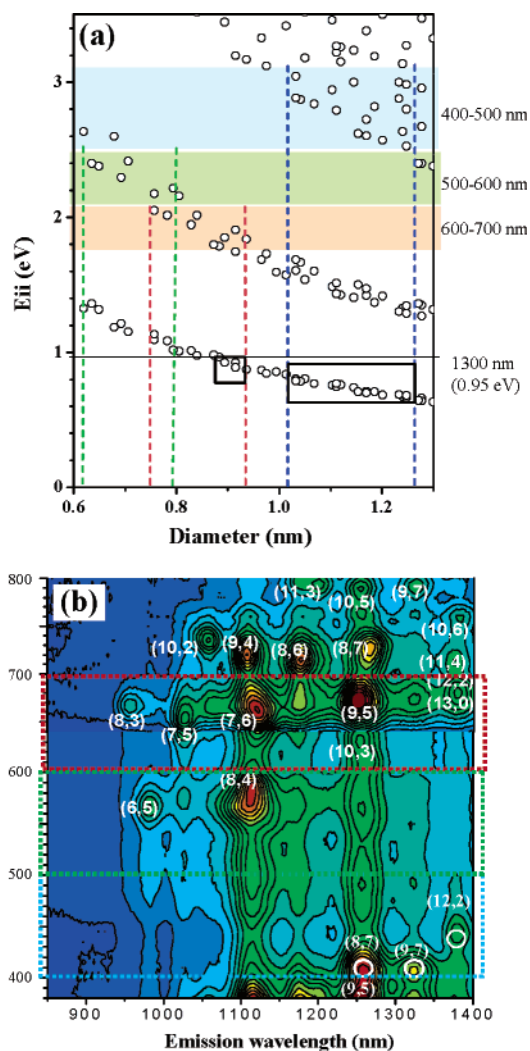


Figure 7. (a) Kataura plot. The light wavelength bands of 400–500, 500–600, and 600–700 nm are shown as color squares. The inserted black boxes indicate SWNTs whose gap energies corresponded to the light wavelength bands of 400–500 nm (2.48–3.1 eV) and 600–700 nm (1.77–2.07 eV) and had emission wavelengths of >1300 nm (<0.95 eV). (b) A contour plot of fluorescence intensity vs excitation and emission wavelengths for SWNT-NaDDBS- D_2O . The (m,n) inserted in Figure 7b was the chiral index of the SWNT assigned using the empirical Kataura plot.³²

The Influence of Light Wavelength. Since the aqueous solution of H_2O_2 or NaDDBS- H_2O_2 did not absorb 400–700-nm light (Figure 6a), their photodegradation by 400–700-nm irradiation was unlikely to happen and thus could not cause the wavelength dependence of the LAOx efficiency as shown in Figure 4. In addition, our experiments revealed little difference in the absorbance of SWNT-NaDDBS- H_2O_2 in the regions of 400–500, 500–600, and 600–700 nm (Figure 6b). It is also unlikely that SWNT light absorption caused the wavelength dependence of the LAOx efficiency seen in Figure 4.

A more reasonable explanation for the wavelength dependence of the LAOx (Figure 4) is as follows. Since H_2O_2 absorbs the light with wavelength of >1300 nm,³⁴ it would absorb the SWNT fluorescence with wavelength >1300 nm. This would enhance the dissociation of H_2O_2 and the generation of hydroxyl radicals,³⁵ which, in turn, would burn out SWNTs. In Figure 7, we show a Kataura plot³⁶ for the diameter range of 0.7–1.3 nm. (In the plot, the color squares indicate the light bands used in LAOx.) The SWNTs in black boxes in Figure 7 had the gap energies corresponding to the LAOx wavelength of 400–500

nm (2.48–3.1 eV) or 600–700 nm (1.77–2.07 eV) and the emission wavelengths at >1300 nm (<0.95 eV). Apparently, the number of SWNT types in the black box corresponding to the 400–500 nm exceeded that corresponding to 600–700 nm. The light wavelength band of 500–600 nm did not correspond to any SWNTs that emitted light with wavelength >1300 nm. This was well reflected in the fluorescence spectra shown as a function of excitation wavelength for SWNT–NaDDBS–H₂O (Figure 7b). We believe that the absorption of the SWNT fluorescence by H₂O₂ was the main factor that caused the photodissociation of H₂O₂, leading to the generation of the hydroxyl radicals.³⁵ This accelerated the oxidation of SWNTs. Thus we consider that the number of SWNT types in the black boxes in Figure 7 could induce the wavelength dependence of the LAOx, 400–500 nm >> 600–700 nm >> 500–600 nm (Figure 4).

Elimination of SWNTs with Diameter Selectivity. Our results also indicated that the change in the quenching coefficients was related to the SWNT diameters (Figure 5). The quenching coefficients of the small-diameter SWNTs were more negative than those of the large-diameter SWNTs. This means that the small-diameter SWNTs were burnt out more easily than the large-diameter ones, which is consistent with the previous reports.^{19–21} Figure 5 also suggested that the SWNTs with larger diameters (>0.97 nm) burnt out more remarkably than those with moderate diameters (0.9–0.97 nm). We tentatively think that H₂O₂ entered inside the SWNTs when their diameters were large (>0.97 nm), and the photodissociation proceeded more efficiently through the absorption of SWNT fluorescence because of the short distance between the SWNT wall and H₂O₂. Thus the SWNT burning by the LAOx became more efficient when the SWNT diameter was large.^{37,38–39} Raman spectra and absorption spectra would be helpful for determining the structure of the SWNTs removed by the LAOx, but they could not be properly measured in this study. The charge transfer between SWNTs and H₂O₂ influenced the Raman spectra of the SWNTs, and the absorption measurement baseline changed with the duration of the LAOx due to the variation of the contents of H₂O₂ and NaDDBS in the SWNT–NaDDBS–H₂O₂.

Conclusion

We have investigated the changes in the fluorescence spectra of individual SWNTs induced by LAOx. We could confirm our previous result that the light irradiation can accelerate the oxidation of SWNTs with H₂O₂.²² Since the fluorescence spectra of SWNTs quenched by LAOx could not be restored by pH adjustment, we believe that SWNTs were burnt out by the LAOx. The LAOx efficiency depended on the irradiating light-wavelength in the order of 400–500 nm >> 600–700 nm >> 500–600 nm > no light. We believe that the absorption of the SWNT fluorescence by H₂O₂ was the main factor that caused the photodissociation of H₂O₂ and the generation of the hydroxyl radicals.³⁵ This accelerated the oxidation of SWNTs. The dependence of LAOx on the wavelength was explained with the number of SWNT types that emit the fluorescence with wavelength >1300 nm by which H₂O₂ was likely to be photodissociated.

The effect of LAOx depended on the SWNT diameters. It was interesting that the SWNTs with larger diameters (>0.97 nm) were burnt out more remarkably than those with moderate diameters (0.9–0.97 nm). This would reflect that H₂O₂ entered inside the SWNTs, and enhanced the SWNT burning by the LAOx through the photodissociation of H₂O₂ caused by absorbing the SWNT fluorescence efficiently due to the short distance between the SWNT walls and H₂O₂.

Supporting Information Available: Fluorescence spectra of SWNTs after the LAOx without surfactant. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Because the aqueous solution of NaDDBS–H₂O₂ does not absorb the light in 400–700 nm (Figure 6a), it is unusual that the light irradiation enhanced the oxidation or decomposition of NaDDBS–H₂O₂. We tentatively think, when NaDDBS was oxidized by H₂O₂, it might form the intermediate oxides, which absorbed the visible light and then accelerated the further decomposition of NaDDBS. Besides SO₄²⁻ and CO₂/H₂O, the product of oxalic acid might be considered as another reason for the pH decrease

because Ashokkumar et al. reported that NaDDBS might decompose and generate oxalic acid [Ashokkumar, M.; et al. *Aust. J. Chem.* **2003**, *56*, 1045].

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