Photo-induced Aggregation of Single-walled Carbon Nanotubes from Dispersion by Using a Photochromic Dispersant

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Dipropylheterocoerdianthrone (DPHCD) was found to be a potential photo-reactive dispersant of single-walled carbon nanotubes (SWNTs). DPHCD was able to well disperse SWNTs in chloroform. DPHCD is easily photo-oxidized by the irradiation of visible light to form the endoperoxide with a bent structure under oxygen or air atmosphere. Then, SWNTs were photo-precipitated from the DPHCD/SWNTs dispersion. The precipitation was able to disperse again after the photochromic reaction to turn back DPHCD from the endoperoxide and sonication. Such photo-induced precipitation was also observed in DPHCD/SWNTs complex film. The SWNTs precipitates were analyzed by FT-IR and Raman spectra measurements, and discussed about selectivity of DPHCD on chirality, and elimination of the dispersant.

Keywords: Aggregation, Photochromism, Singlet oxygen, Endoperoxide, Carbon nanotube, π-π stacking, Functional dispersant

1. Introduction

Carbon nano-materials are notable for their specific physical properties, with carbon nanotubes [1] in particular being potentially useful. However, it is quite difficult to individually disperse nanotubes in common solvents because of their strong interactions, especially π-π stacking interaction. This represents a significant obstacle to purify carbon nanotubes and fabricate carbon nanotube devices, and the techniques for individually dispersing carbon nanotubes have being actively researched. For example, the individual dispersion of single-walled carbon nanotubes (SWNTs) without molecular modification can be achieved by adsorption of surfactants [2-6] or ionic liquid surfactants [7] in aqueous or organic solvents [8]. Block co-polymers [9] and DNA [10] can also produce the individual dispersion of SWNTs. Such compounds, which enable the dispersion of SWNTs, are termed SWNTs dispersants. Unlike the case of chemical modification, the action of such dispersants can preserve the intrinsic physical properties of the SWNTs and some π-surfactants [11] are expected both to efficiently remove impurities from SWNTs and to sort them according to specific feature such as electric properties. Attempts have been made to utilize such dispersant/SWNTs complexes in the development of functional material, such as the SWNTs transparent conducting film [12].

In addition, among the SWNTs dispersants, some reactive aromatic compounds [13,14] and polymers [15-17] have been reported to control SWNTs dispersion and aggregation by their photochemical or thermal reactions. Condensed aromatic groups such as anthracene or pyrene having π-π interaction with SWNTs are also involved in SWNTs dispersants. Such smaller molecules with π conjugation have a potential to refine crude SWNTs. Lu et al. proposed a purification method for removing residual metal catalysts and carbonaceous impurities, using 1-pyreneacetic acid in aqueous dispersion liquid [13].

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Heterocoerdianthrone (dibenzo[a,j]perylene-8,16-dione) (HCD) and its derivatives are well known as components in photo-reversible systems between the visible and ultraviolet regions. They are capable of forming endoperoxides (HCDPOs), which have significant thermal stability [18,19]. In this photochromic reaction, singlet oxygen (\(^{1}\text{O}_2\)) is initially generated by the triplet sensitization reaction of HCD [20]. The addition of \(^{1}\text{O}_2\) to HCD produces a colorless endoperoxide product. The HCDPO reverts to HCD, eliminating the oxygen molecule, under UV irradiation or by adding heat. Thus, the HCD derivatives have been attempted to be utilized in optical switching and memory [21]. On the other hand, the HCD derivatives, which have large \(\pi\)-conjugation can be adsorbed on the surface of CNTs through a \(\pi-\pi\) stacking interaction mechanism. By introducing hexyl group into the HCD structure, the solubility of dihexyl-HCD was improved, and it dispersed SWNTs in organic solvent and formed SWNTs films [22].

It was also found here that dipropylheterocoerdianthrone (DPHCD), which has shorter alkyl side chains than dihexyl-HCD does, acts as photo reactive dispersants (PRD) photo-switching of their aggregation. The photo-precipitation of SWNTs from DPHCD/SWNTs complex was performed both in the dispersion liquid and especially in the film. Moreover, we showed that DPHCD was able to be recycled in the reverse reaction. From the result of the Raman spectra, it was shown that DPHCD has a possibility to selectively disperse semiconducting SWNTs.

2. Materials and methods

2.1. Preparation of DPHCD and DPHCDPO

The DPHCD (dipropylidenbenzo[a,j]perylene-8,16-diones) was prepared from anthraquinone-1,5-dicarboxyl dichloride and the propylbenzene with aluminum chloride in nitrobenzene in accordance with the literature [18,19,23]. The product was purified as follows. After extraction with toluene from the residue removed nitrobenzene by steam distillation, the solution was washed with 1% ammonia water and evaporated. The colored solid was refined by silica gel column chromatography with an eluent of ethyl acetate/hexane (1:6 v/v). The obtained product was then recrystallized from the chloroform/hexane (3:1 v/v) solution. \(^{1}\text{H}-\text{NMR} (\text{CDCl}_3, 400 \text{ MHz}): \delta 1.03 \text{ (t, 6H, } J = 7.3 \text{ Hz, } \text{CH}_2\text{CH}_2\text{CH}_3), 1.80 \text{ (hept, 4H, } J = 7.5 \text{ Hz, } \text{CH}_2\text{CH}_2\text{CH}_3), 2.80 \text{ (t, 4H, } J = 7.7 \text{ Hz, } \text{CH}_2\text{CH}_2\text{CH}_3), 7.58 \text{ (dd, 2H, } J = 8.3, 2.0 \text{ Hz), 7.80 (dd, 2H, } J = 7.4, 8.8 \text{ Hz), 8.10 (d, } J = 8.4 \text{ Hz), 8.38 (s, 2H), 8.80 (dd, 2H, } J = 7.3, 0.93 \text{ Hz), 8.99 (d, 2H, } J = 8.8 \text{ Hz), HRMS-ESI (} m/z): [M+H]^+ \text{ Calcd. for } C_{34}H_{27}O_2 467.2006; \text{ found, 467.2002.}

The DPHCDPO is the endoperoxide of DPHCD. It was prepared by sufficient photo-irradiation of the DPHCD solution under an oxygen atmosphere and refined by column chromatography in a dark environment. \(^{1}\text{H}-\text{NMR} (\text{CDCl}_3, 400 \text{ MHz}): \delta 1.04 \text{ (t, 6H, } J = 7.2 \text{ Hz, } \text{CH}_2\text{CH}_2\text{CH}_3), 1.80 \text{ (hept, 4H, } J = 7.5 \text{ Hz, } \text{CH}_2\text{CH}_2\text{CH}_3), 2.83 \text{ (t, } J = 7.8 \text{ Hz, } \text{CH}_2\text{CH}_2\text{CH}_3), 7.34 \text{ (dd, 2H, } J = 7.6, 1.2 \text{ Hz), 7.45 (t, 2H, } J = 7.8 \text{ Hz), 7.84 (d, 2H, } J = 8.0 \text{ Hz), 8.19 (dd, 2H, } J = 8.0, 1.2 \text{ Hz), 8.38 (d, 2H, } J = 1.8 \text{ Hz), HRMS-ESI (} m/z): [M+H]^+ \text{ Calcd. for } C_{34}H_{27}O_4 499.1904; \text{ found, 499.1985.}

2.2. Dispersion of SWNTs and photo-irradiation

The dispersion of SWNTs using DPHCD was performed as follows. First, sonication to disperse the SWNTs in solvent was performed as described in the literature [3,24]. SWNTs (Aldrich, SWNT CG100, 2.5 g dm\(^{-3}\)) and DPHCD in chloroform was treated in an ultrasonic bath for 1 h, followed by direct sonication with an ultrasonic homogenizer (SMT Co., Ltd., UH-150) for 1 h. The mixture was then centrifuged for 30 min (10 k rpm 7930 \(\times g\), after which, the supernatant was obtained and the UV-visible-NIR spectra were observed. The dispersion was dripped onto hydrophobic treatment glass or polyimide film, and dried to form a film of the DPHCD/SWNTs complex. Photo-irradiation of the dispersion and film samples was provided by LED light sources (Omicron LEDMOD470 and 590, Tokyo Instruments) at the wavelength of 470 nm and 590 nm.

2.3. Re-dispersion of SWNTs

The dispersion and photo-irradiation was performed by means of the method described above. Then, the obtained dispersant was treated by two methods to reproduce DPHCD from DPHCDPO; 1) UV irradiation: the dispersion was exposed by ultrahigh pressure mercury lamp (USHIO SP5-250DB) for 20 min through 365 nm bandpass filter to avoid irradiation of visible light; 2) Heating: the dispersion was refluxed for 5 h in the dark environment. After both procedures, the dispersion was sonicated again in ultrasonic bath for 1 h and measured by UV-vis-NIR spectrometer.

2.4. Measurements

The UV-vis-NIR absorption spectra were recorded on a JASCO V-670 DS spectrophotometer. The
optical path length was 1 cm. The IR spectra were used on a HORIBA FT-200 spectrometer. The Raman spectra were investigated on a JASCO RMP-510 spectrometer, and the 1H-NMR is measured on a JEOL LA-400 spectrometer (400 MHz).

3. Results and discussion

Based on the photochromic reactions between DPHCD and DPHCDPO and the discussion of molecular structure changes, we revealed here the photo-induced precipitation from the DPHCD/SWNTs dispersion, and re-dispersion of the precipitate. It is expected for such functional dispersant to have any selectivity in dispersion or precipitation processes. Analyses of the precipitate took place for the purpose.

3.1. The molecular modeling of DPHCD and DPHCDPO

The photochromic reaction of DPHCD and DPHCDPO based on the addition and elimination of singlet oxygen simultaneously alters the aggregation state with other π-conjugation compounds. The chemical structure and molecular models of DPHCD and DPHCDPO are shown in Fig. 1. DPHCDPO is reduced π-conjugation from DPHCD, due to the adding O2. In addition, the DPHCDPO are considered to have a bent structure at the central ring as shown in Fig. 1. The twisted angle between the moieties in HCDPO has been estimated to be about 55.5°, in contrast to the 19.2° angle in HCD [18]. The bent structure and reduced π-conjugation are expected to induce a break of π-π stacking between HCD derivatives and CNTs or graphenes. This gives an unique photo-switching mechanism, which alters the aggregation state.

3.2. Photochromic reaction of DPHCD

DPHCD are well soluble in chloroform, and showed strong absorption in visible region. By the irradiation of the visible light at 590 nm under air atmosphere, these strong absorption peaks were...
reduced, and those peaks reverted back by the irradiation of the UV light as shown in Fig. 2. In this photo-reversible system, DPHCD sensitizes oxygen molecule to generate \(^{1}\text{O}_{2}\) in solution, and the \(^{1}\text{O}_{2}\) reacts DPHCD self to the endoperoxide, DPHCDPO, which does not have absorption in visible region. The DPHCDPO reverts to DPHCD as shown in Fig. 2 (b) by the UV irradiation. However, in this photo-reaction, both of DPHCDPO and DPHCD absorb the UV light, and excited endoperoxides might have other reaction paths [26].

3.3. Dispersion of DPHCD/SWNTs

The UV-vis-NIR spectra are useful to know the chirality and aggregation of SWNTs. As shown in Fig. 3, the dispersion of SWNTs using DPHCD has broad absorption with specific peaks over 650 nm, which is not the DPHCD absorption. The characteristic peaks are due to van Hove transition, indicating the presence of SWNTs dispersed individually [24]. The van Hove singularities at the specific wavelength correspond to the chirality with chiral number \((n, m)\) [27]. In Fig. 3, the peaks at 660 nm can be assigned as \((7, 5)\), \((7, 6)\), 735 nm as \((8, 6)\), \((8, 7)\), \((9, 4)\), 973 nm as \((6, 5)\), and 1160 nm as \((7, 6)\), respectively. However, the peaks were not sharp but clearly observed. Consequently, it shows that DPHCD individually disperse SWNTs but there are bundled SWNTs in the dispersion.

Fig. 3. UV-Vis-NIR spectra of DPHCD \((1.0 \times 10^{-5} \text{ mol dm}^{-3})\) (blue) and DPHCD/SWNTs (red) in chloroform after sonication and centrifugation.

3.4. Photo-induced precipitates of SWNTs

By the irradiation of the visible light, photo-precipitation of SWNTs occurred from the dispersion of DPHCD/SWNTs. In Fig. 4, a decrease in absorption of SWNTs in the dispersion liquid was observed after irradiation under 470 nm LED light with oxygen atmosphere. It is considered that this change was induced by the photochemical reaction to form DPHCDPO from DPHCD. DPHCD adsorbed on the surface of SWNTs were released as DPHCDPO, losing \(\pi-\pi\) interaction. Then SWNTs are thought to spontaneously aggregate and precipitated from dispersant. Black precipitates were obtained from the red-colored dispersion, as shown in the photograph inserted in Fig. 4.

One of the advantages of photochemical technology is that it enables to commence with photo-irradiation in a restricted space. Primitive demonstrations are shown in Fig. 5. Figures 5 (a) and (b) show a photo-irradiated sample. In this experiment, half of the vessel was masked, and the red colored dispersion was then irradiated by the LED light at 470 nm. Black particles appeared in the irradiated section. Moreover, it is also possible to form a solid film from the DPHCD/SWNTs dispersion, and then to induce photo-precipitation of SWNTs in the film. Figures 5 (c) and (d) show a photo-patterning in the DPHCD/SWNTs film. The sizes of precipitates were in the range of 5-30 \(\mu\text{m}\) in the irradiated section, and less than 5 \(\mu\text{m}\) in the non-irradiated section. Because it was difficult to perfectly shield against visible light in this observation, a small precipitation might occur in the non-irradiated section.

As shown in Figs. 4 and 5, the photo-precipitation of SWNTs from the DPHCD/SWNTs dispersion was observed not only in the liquid but also in the film. Regarding the solid materials of the dispersant/SWNTs complex, an interesting report suggested that SWNTs were found to be oriented in
discotic ionic liquid crystals acting as a dispersant [28]. In the present study, the photochemical switching of the π-π stacking initiates the aggregation of SWNTs even in the solid film. In the film as well, the aggregated SWNTs did not become re-soluble through the regeneration of DPHCD in the photochromic reaction. However, it is possible for photochromic dispersants to be recycled, and a host of photochromic reactions may be designed using photo reactive dispersants (PRDs).

Fig. 5. Photograph of photo-precipitation from the dispersion of DPHCD/SWNTs (1.3 × 10⁻² mol dm⁻³) in chloroform (a), (b). The half-section (A) was irradiated by 470 nm LED light (3.16 J cm⁻²) under oxygen atmosphere. Photo-induced precipitation of DPHCD/SWNTs solid film in half (the left side) of the film irradiated with 590 nm LED light (2.96 J cm⁻²) in an oxygen atmosphere (c), (d).

3.5. Re-dispersion of SWNTs using photochromic reaction of DPHCD

HCDs are able to regenerate from HCDPO through UV irradiation and heating [20]. Considering this feature, it is expected that the SWNTs which has precipitated once, can be re-dispersed using this dispersant. Figures 6 and 7 show the absorption change through re-dispersion procedure by UV irradiation and heating, respectively. After the “first” dispersion procedure, the increase of absorption above 650 nm was observed. It is presumably due to existence of SWNTs in the dispersion. And then, these were decreased after visible light irradiation because SWNTs precipitated and went out from the dispersant. The result up to this point is almost the same as that of Fig. 4. Furthermore, the reproduction procedure of DPHCD was performed by UV irradiation and heating, followed by a “second” dispersion procedure by sonication. In both Figs. 6 and 7, we were able to observe the recovery of absorption. The absorption of “reproduced by UV” sample almost perfectly recovered to that of the “first” dispersion. On the other hand, the absorption of the “reproduced by heating” sample did not recover so much. Chloroform is a comparatively low-boiling point solvent, so the reproduction of HCD from HCDPO was not facilitated in spite of 5 h reflux. By considering these results, DPHCD is able to re-disperse SWNTs through its reversible photochromic reaction. Scheme 1 summarized these procedures and reactions.

Fig. 6. Re-dispersion of SWNTs using the UV-light irradiation process. UV-Vis spectra of (1) DPHCD (1.0 × 10⁻³ mol dm⁻³) in chloroform, (2) DPHCD/SWNTs after dispersion procedure in chloroform, (3) DPHCD/SWNTs after irradiation with 590 nm LED light (1.63 J cm⁻²), and (4) DPHCD/SWNTs after irradiation with an ultra-high-pressure mercury lamp and sonication.
Fig. 7. Re-dispersion of SWNTs by using heating process. UV-Vis spectra of (1) DPHCD (1.0 × 10⁻³ mol dm⁻³) in chloroform, (2) DPHCD/SWNTs after dispersion procedure in chloroform, (3) DPHCD/SWNTs after irradiation with 590 nm LED light (1.63 J cm⁻²), and (4) DPHCD/SWNTs after reflux for 5 h.

Scheme 1. Dispersion and re-dispersion of SWNTs by DPHCD.

3.6 Analyses of precipitates by FT-IR spectra and Raman spectra

The FT-IR spectra of the precipitates from the dispersion were measured after filtration and washing with chloroform. Figure 8 shows the FT-IR spectra of precipitate, as-provided SWNTs, DPHCD, and DPHCDPO. The peaks of aromatic ketone appear at 1650 cm⁻¹ and 1680 cm⁻¹ for DPHCD and DPHCDPO respectively. Those peaks were not observed in spectra of as-provided SWNTs and precipitates. This result suggests that DPHCDPO, which is generated by photo-irradiation, went out from surface of SWNTs completely. However, there remains the possibility that a small amount of DPHCD is strongly adsorbed by SWNTs.

Raman spectra of as-provided SWNTs and precipitated SWNTs through photo-reaction are shown in Fig. 9. Basically, three features appeared when SWNTs are excited at specific wavelengths, 1) Radial breathing mode (RBM) which corresponds to stretching vibration of C atom in the direction of the diameter; 2) Tangential mode (G band) which corresponds to in-plane stretching vibration of six-membered ring of C atom. It subdivides to G⁺ band and G⁻ band in the case of SWNTs, where G⁺ band and G⁻ band represent longitudinal optical phonons and transverse optical phonons of graphite, respectively; 3) Disorder-related mode (D band) which corresponds to defects which exist in carbon materials. We focused here on the ratio of G⁻ band intensity to G⁺ band intensity (I_G⁻/I_G⁺). Since I_G⁻/I_G⁺ value indicates the degree of metallic SWNTs existence, some studies which discuss the selectivity of dispersant to specific SWNTs has been reported [8]. Meanwhile, the ratio of D band intensity to G band intensity (I_D/I_G) value is helpful to determine the degree of impurity such as defect of SWNTs and amorphous carbon [29]. In Fig. 9, the G⁻ band intensity of precipitated SWNTs decreased compared with that of as-provided SWNTs. The value of I_G⁻/I_G⁺ decreased from 0.523 to 0.448. From this result, it might be said that DPHCD has inferior affinity to metallic SWNTs relative to semiconducting SWNT. Thus, certain amounts of metallic SWNT were excluded through dispersion procedure such as centrifugation. In addition, a slight increase of I_D/I_G value was observed between the two samples. The value of I_D/I_G increased from 0.121 to 0.132. It is considered that SWNTs was damaged through 2 h ultra-sonication. It was expected that I_D/I_G value of precipitated SWNTs is smaller than that of as-provided SWNTs because impurities such as amorphous carbon were eliminated through the dispersion procedure. However, a contrary result was provided. Consequently, I_D/I_G value increased...
slightly. Based on this, it is predicted that the effect of purification through dispersion and precipitation procedure and the effect of damage through sonication procedure are competitive, and the latter overcomes the former.

The results of the FT-IR analysis of the precipitates suggest that it is possible to obtain SWNTs precipitates without dispersant components, by mean of this photo-induced precipitation method involving photochromic dispersion. Though many kinds of SWNTs dispersants, such as polymer materials, surfactants and aromatic compounds, have been discovered and developed, it has hitherto been difficult to separate these from the SWNTs surface, due to their strong interactions with the SWNTs. The compounds discussed in the present study, however, show potential for overcoming this difficulty, as they become separable over the course of the procedure.

On the other hand, we have not gotten any definitive evidence about the selectivity of DPHCD on chirality and the electric property of SWNTs obtained by the Raman spectra. However, there is possibility that DPHCD can disperse semiconducting SWNTs selectively, in terms of the change of \( I_G/I_G+ \) values between as-provided SWNTs and precipitated SWNTs.

4. Conclusion

DPHCD clearly acted as a SWNTs dispersant in chloroform. Photo-induced precipitation took place both in the SWNTs dispersion liquid and in the solid film of the complex. It was found that precipitated SWNTs were free from dispersants. The photochemical reaction of DPHCD, which induces the change in \( \pi-\pi \) interaction, supports the notion of photochromic dispersants as a promising form of PRD for nanocarbon materials in organic solvents. Furthermore, DPHCD can be reused as a dispersant through its reversible photochromic reaction. It is a great advantage in the field of SWNTs dispersants. Photo-induced precipitation appears to have considerable potential as a technique for fabricating and purifying nanocarbon materials.

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