



Dispersibility Tuning of Single-Walled Carbon Nanotube by Photoresponsive Dispersants

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ABSTRACT

We demonstrated the dispersibility tuning of single-walled carbon nanotubes (SWCNTs) by the photoisomerization of azobenzene-derived dispersants. Upon irradiation with UV and visible light, the SWCNT/dispersant exhibited rapid switching between dispersion and precipitation.

Keywords: photoisomerization, azobenzene, carbon nanomaterials

Introduction

Single-walled carbon nanotubes (SWCNTs) have attracted immense attention in various applications owing to their unique mechanical, optical, and electrical properties.¹ For example, metal/SWCNT composites are used as cable materials,² and thin films of SWCNTs are used as flexible transparent conductive films and transistors.³ In order to fabricate high-performance SWCNT-based devices, it is important to not only ensure that the SWCNTs are of high quality, but also to remove the organic additives (*e.g.*, solvents and dispersants) used during the fabrication process.⁴ In particular, the presence of residual organic components in SWCNTs adversely affects the optical and electrical properties of SWCNT-based devices.

Recently, stimuli-responsive dispersants (*e.g.* light-,⁵ heat-,⁶ pH-,⁷ and solvent-responsive⁸) have been investigated for the purification of SWCNTs and removal of organic components from SWCNT-based devices during the fabrication

process. In our previous study, we developed photoresponsive dispersants containing stilbene and azobenzene cores as the photoresponsive moieties. A dispersion of SWCNT/stilbene (or azobenzene) hybrids in water undergoes precipitation upon irradiation with UV light.^{9,10} In this study, we developed a new photoresponsive dispersant, which could disperse SWCNTs in polar organic solvents. Moreover, the SWCNT/dispersant hybrids exhibited rapid switching between dispersion and precipitation upon irradiation with UV and visible light.

Experimental Section

The reagents and solvents were purchased from Aldrich, Wako chemical, Tokyo Chemical Industry, CIL, and Merck. SWCNT, which were synthesized from a high-pressure carbon monoxide method (HiPco) was purchased from Sumitomo Corporation. UV-vis-NIR spectra were measured with V-670 (JASCO) using quartz or glass cells. UV and visible lights were irradiated by UV-LED (HOYA Candeco Optronics, EXECURE H-1 VC II) and Super-high pressure mercury lamp (USHIO, E016 with optical cut filter), respectively. 4-(1H-Imidazol-1-yl)aniline (1.5 g, 9.4 mmol) and triethylamine (2.0 g, 19.8

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mmol) dissolved dichloromethane (dehydrated, 20 mL) was added to a solution of 4,4'-azodibenzoyl dichloride (1.0 g, 3.3 mmol) in dichloromethane (dehydrated, 30 mL). The mixture was stirred for 12 hours in room temperature. The precipitates was filtered, washed with dichloromethane, and dried in vacuo, to give **1** (1.7 g, 93%) as a yellow powder. $^1\text{H-NMR}$ (400 MHz, Pyridine- d_5 , δ): 8.11-8.15 (m, 8H, ArH), 8.21 (m, 4H, ArH), 8.32 (s, 2H, ArH), 8.45 (m, 4H, ArH), 8.56 (m, 4H, ArH), 11.4 (s, 2H, NH).

The obtained **1** (1.7 g, 3.1 mmol) and methyl trifluoromethanesulfonate (2.0 g, 12 mmol) in dimethylformamide (200 mL) was stirred for 48 hours at room temperature. The solution was added to acetone. Obtained precipitates were filtrated and washed with acetone to give **AB2** as a yellow powder (2.4 g, 89%). ν_{max} (KBr)/ cm^{-1} 3159 (ν_{CH} , Ar), 3113 (ν_{CH} , Ar), 1667 ($\nu_{\text{C=O}}$, amide), 1518 (σ_{NH}). λ_{max} (propylene carbonate)/nm 340 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, 43100). $^1\text{H-NMR}$ (400 MHz, DMSO- d_6 , δ): 3.95 (s, 6H, CH_3), 7.78 (m, 4H, ArH), 7.94 (m, 4H, ArH), 8.04-8.11 (m, 8H, ArH), 8.22-8.27 (m, 4H, ArH), 9.70 (s, 2H, ArH), 10.7 (s, 2H, NH).

Results and Discussion

We synthesized two photoresponsive dispersants: **AB1** (water-soluble) and **AB2** (soluble in polar organic solvents). **AB1** was synthesized according to the procedure given in a previous report.¹⁰ **AB2** was synthesized in two steps with an overall yield of 85%. As shown in Fig. 1, an aqueous solution of **AB1** showed a strong absorption band at 330 nm. On the other hand, a propylene carbonate (PC) solution of **AB2** showed a strong absorption band at 340 nm. These absorption bands correspond to the π - π^* transition of *trans*-azobenzene. Upon UV irradiation (365 nm, 150 mW/cm^2 , 30 s), the intensity of these absorption bands decreased, while that of the absorption bands at 423 and 440 nm, which correspond to the n - π^* transition of *cis*-azobenzene, increased. This indicates that the UV irradiations caused the photoisomerization of azobenzene. The *cis*-isomer ratios of **AB1** (90%) and **AB2** (57%) in the photostationary state were determined by $^1\text{H-NMR}$ spectroscopic measurements. From the UV-Vis absorption spectra of *cis*-**AB1** and *cis*-**AB2**, the rate constant of the *cis*-to-*trans* thermal isomerization (k_{c-t}) reactions of **AB1** and **AB2** were determined to be 6.65×10^{-7} and $2.66 \times 10^{-6} \text{ s}^{-1}$, respectively, at 25 °C (Fig. 2). These values indicate that *cis*-**AB1** and *cis*-**AB2** exhibited sufficient thermal stability. In contrast, upon

irradiation with visible light (436 nm, 25 mW/cm^2 , 60 s), the features in the absorption spectra of the *cis*-forms of **AB1** and **AB2** changed immediately to those of their *trans*-forms.

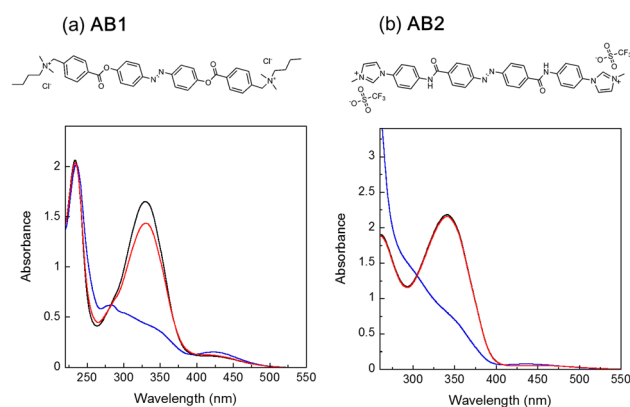


Figure 1. Chemical structures and UV-vis spectra of (a) **AB1** ($5.0 \times 10^{-5} \text{ M}$) in H_2O and (b) **AB2** ($5.0 \times 10^{-5} \text{ M}$) in PC at 25 °C. Black line: before UV irradiation, blue line: after UV irradiation, and red line: after visible-light irradiation.

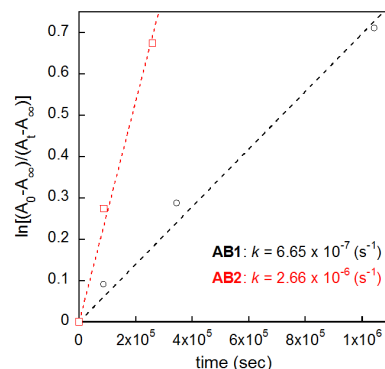


Figure 2. Plots of the first-order *cis*-to-*trans* isomerization of **AB1** (black circle) and **AB2** (red square) after UV irradiation at 25 °C.

Using **AB1** and **AB2**, we obtained well-dispersed solutions of SWCNTs in water and PC, respectively. These dispersions were prepared according to a previous report.¹⁰ We could easily tune the dispersibility of SWCNTs by irradiation with UV and visible light. Upon UV irradiation (365 nm, 150 mW/cm^2 , 10 min), the SWCNT/**AB1** (1:1.5) and SWCNT/**AB2** (1:3) dispersions changed into precipitates along with the *trans*-to-*cis* photoisomerization of azobenzene (Fig. 3). These precipitates converted back to the SWCNT/**AB1** and SWCNT/**AB2** dispersions upon irradiation with visible light (436 nm, 25 mW/cm^2 , 20 min) followed by sonication (80 W, 37 kHz, 5 min).

Over the three dispersion and precipitation cycles under alternate UV and visible light irradiations, only a slight spectral change was

observed (Fig. 3 inset).

The mechanism for this dispersibility switching is proposed here. Figure 4 shows the plausible mechanism for dispersibility switching of the SWCNT/AB1 dispersion. Upon irradiation with UV light, AB1 (adsorbed on the surface of SWCNTs) exhibited a *trans*-to-*cis* photoisomerization. *Cis*-AB1 desorbed from the surface of SWCNTs because of its low-affinity to graphitic structures. The AB1-desorbed SWCNTs showed poor dispersibility in water. Thus, the precipitation of SWCNTs occurred. The resulting SWCNT-precipitated solution underwent a *cis*-to-*trans* photoisomerization upon irradiation with visible light. The *trans*-AB1 so obtained could again adsorb onto the SWCNT surface via the π - π interactions between the planar structure of the azobenzene core and the graphitic structure of SWCNTs. AB2 dissolved in PC also showed a similar behavior.

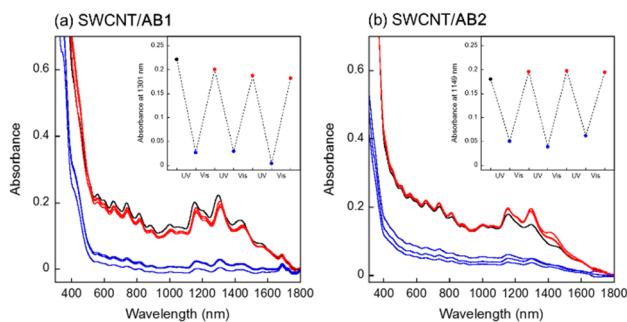


Figure 3. (a) UV-Vis-NIR spectral changes of the photo-irradiated (a) SWCNT/AB1 in a D₂O/ethanol (9 : 1) mixture and (b) SWCNT/AB2 in PC at 25 °C. Black line: without UV irradiation, blue line: after UV irradiation, and red line: after visible-light irradiation and sonication (5 min). The insets show absorbance changes of the SWCNT dispersions before UV irradiation (black circle), after UV irradiation (blue circle) and after visible-light irradiation (red circle).

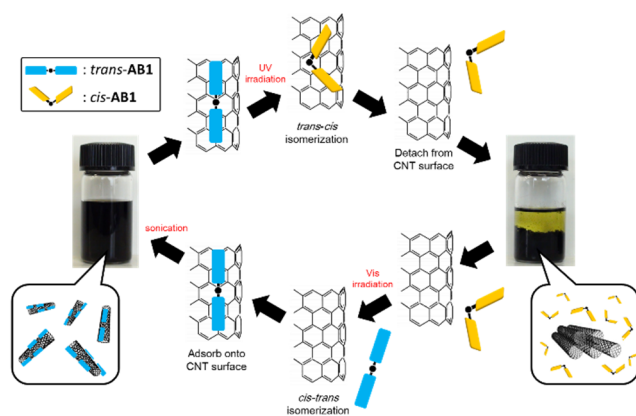


Figure 4. Schematic image of photo induced dispersibility tuning of the SWCNT/AB1 dispersion.

Conclusions

In conclusion, we demonstrated the dispersibility tuning of SWCNTs in water and organic solvents by photoresponsive dispersants. Upon UV and visible light irradiation (for a short time), the SWCNT/dispersant hybrids showed switching between dispersion and precipitation because of the photoisomerization of azobenzene present in the dispersants. We believe that this dispersibility tuning approach can be used for a variety of applications such as the fabrication of high-performance electric SWCNT devices.

Acknowledgments

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