

Aqueous Dispersion of Carbon Nanotubes by Simple Aromatic Molecules: Effects of Aromatic Ring Numbers and Substituted Groups

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Aqueous dispersion of SWNTs was achieved by using simple aromatic molecules as dispersants. Aromatic molecules used in this study were naphthalene, anthracene, and pyrene with or without a carboxyl group. Absorption spectra of SWNTs wrapped with the aromatic molecules exhibited that both the greater number of aromatic rings and the presence of carboxyl groups were required for the dispersion of SWNTs. It was therefore suggested that both π - π interactions between SWNTs and the aromatic molecules, and the hydrophilicity of the aromatic molecules were significant for the dispersion of SWNTs. AFM observations demonstrated that the disentangled SWNTs were prepared from bundled SWNTs by wrapping with the aromatic molecules. Our results will be utilized as basic data for disentanglement and dispersion of SWNTs in water.

SWNTs[1] discovered in 1991 have been emphasized as potential candidates for a large number of applications including health, energy, and the environments, owing to the fascinating mechanical, electrical, and chemical properties[2-5]. However, as-synthesized SWNTs are insoluble in any solvents (especially in water) due to self-aggregating properties caused by strong van der Waals interactions between the SWNT sidewalls. This drawback of SWNTs often has inhibited their applications. Therefore, the disentanglement of SWNTs has been attempted by either chemical reaction-based covalent or physical adsorption based-noncovalent methods. This latter method giving a minimal impact on the original properties of SWNTs has widely been performed by wrapping of SWNTs with surfactants, synthetic polymers, DNAs, nucleotides, peptides, and polysaccharides, followed by the preparation of aqueous SWNTs dispersion through π - π interactions and/or hydrophobic effects[6-12].

Recently, polycyclic aromatic molecules have been utilized to disperse SWNTs in water due to their π electron rich structures that enable to interact with SWNT surfaces. Especially, pyrene derivatives bearing various substituted groups such as primary and tertiary amino, aldehyde, hydroxy, and sulfate groups were

demonstrated to effectively disperse SWNTs in aqueous phase[8]. Among them, a derivative of pyrene, trimethyl-(2-oxo-2-pyrene-1-yl-ethyl)-ammonium bromide, is well known as an excellent dispersant in aqueous phase against SWNTs[13]. Although a carboxylic derivative of pyrene, PCA, was also utilized to disperse and functionalize SWNTs for preparation of polymer composites without substantial cutting and introduction of defects against SWNTs[14], such simple carboxylic derivatives of aromatic molecules have not been systematically studied. In this study, we systematically compared the capabilities of simple aromatic molecules for dispersing SWNTs in water (Figure 1a). The derivatives used in this study are naphthalene, anthracene, pyrene, and their carboxylic derivatives such as NCA, ACA, and PCA (Figure 1b). Absorption spectra exhibited that the greater numbers of aromatic rings and the presence of carboxylic acids were effective for the dispersion of SWNTs in water. AFM observations displayed excellent dispersion of SWNTs with increasing the number of aromatic rings for carboxylic derivatives. Our results will be utilized as basic data to construct well-dispersed hybrid nanomaterials of SWNTs for future applications.

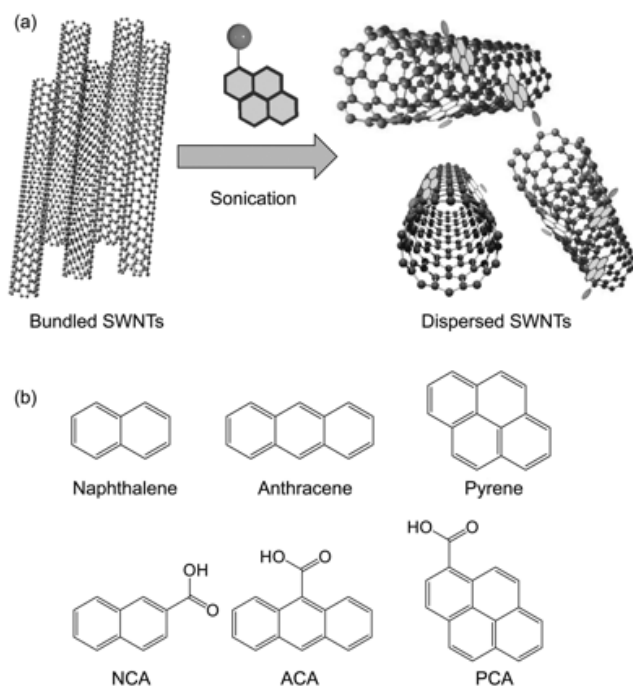


Figure 1. (a) A schematic illustration of dispersion of SWNTs from bundled SWNTs by aromatic molecules. (b) Chemical structures of aromatic molecules used in this study.

Naphthalene, anthracene, and pyrene were purchased from Nacalai Tesque. NCA and ACA were purchased from Sigma-Aldrich. ACA was purchased from Tokyo Chemical Industry (TCI). Dispersion of SWNTs by the aromatic molecules in water was performed as previously described[14,15] with modification of centrifugation conditions. Solutions (1 mL) of aromatic molecules dissolved in methanol (2 mM) was added into 2 mL of aqueous solutions containing 1.0 ± 0.1 mg of pristine HiPco SWNTs (Unidym Inc.). Then, the mixed solution was sonicated for 2 h by a Branson Advanced Sonifier 250 AA (output power: 20W) with a water cooling system, followed by centrifugation at 2000 rpm for 15 min. The precipitates were washed with 2 mL of water, and then dispersion was sonicated for 5 min. This procedure was repeated for 3 times to eliminate excess aromatic molecules and to exchange the solvent from methanol to water. The resultant precipitates were re-dispersed in water by the sonication for 2 h, followed by centrifugation at 7400 rpm for 30 min to remove the any insoluble SWNTs. When SDBS was used as a dispersant of SWNTs for the control experiment, 1.0 ± 0.1 mg of the SWNTs were added to 2 mL of SDBS solution (2 mM), and the mixed solution was sonicated for 2 h under the same condition, followed by the centrifugation process. The supernatants of aromatic molecules/SWNTs showed the white gray color, suggesting that aqueous SWNT dispersion was successfully achieved by wrapping with aromatic molecules. Ultrapure water with more than $18.2 \text{ M}\Omega \text{ cm}$ was supplied by the Milli-Q

system (Merck Millipore), and was used throughout all experiments.

To investigate the dispersion capability of the aromatic molecules for SWNTs, ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectra of the supernatants were recorded on V670 (JASCO). The absorption spectra indicated that SWNTs could be dispersed in water by wrapping with aromatic molecules (Figure 2a). SDBS, a famous surfactant to disperse SWNTs well, was used as a reference. The absorption spectra of dispersed SWNTs by aromatic molecules showed a series of sharp transition as oscillations, which can be attributed to different chiralities of multitudinous SWNT species[3], indicating chirality-independent dispersion. In contrast, the typical oscillations from the SWNT dispersions were hardly observed in the absence of aromatic molecules. The absorbance values at 660 nm that correspond to the amounts of the dispersed SWNTs [10,16] were compared (Figure 2b). The order of dispersion amounts was $\text{PCA} > \text{SDBS} \approx \text{ACA} \approx \text{Pyrene} \approx \text{Naphthalene} > \text{Anthracene} > \text{NCA}$. It was suggested that PCA was the best aromatic molecule as dispersants for SWNTs among all of molecules used in this study. Comparison of the dispersion amounts of SWNTs by PCA, ACA,

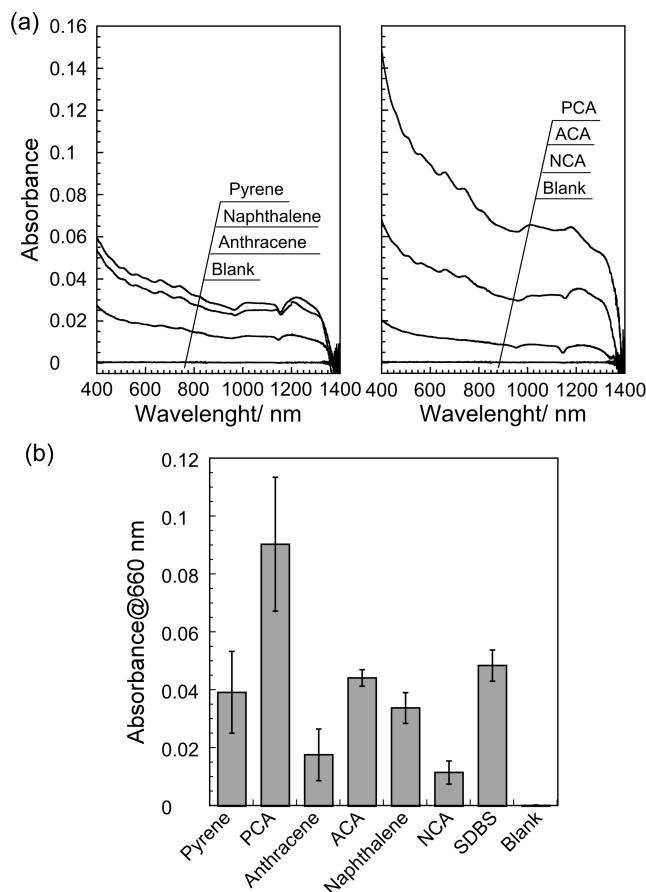


Figure 2. (a) Absorption spectra of SWNTs dispersed by aromatic molecules in aqueous phase. (b) Comparison of the dispersion capabilities of the aromatic molecules for SWNTs.

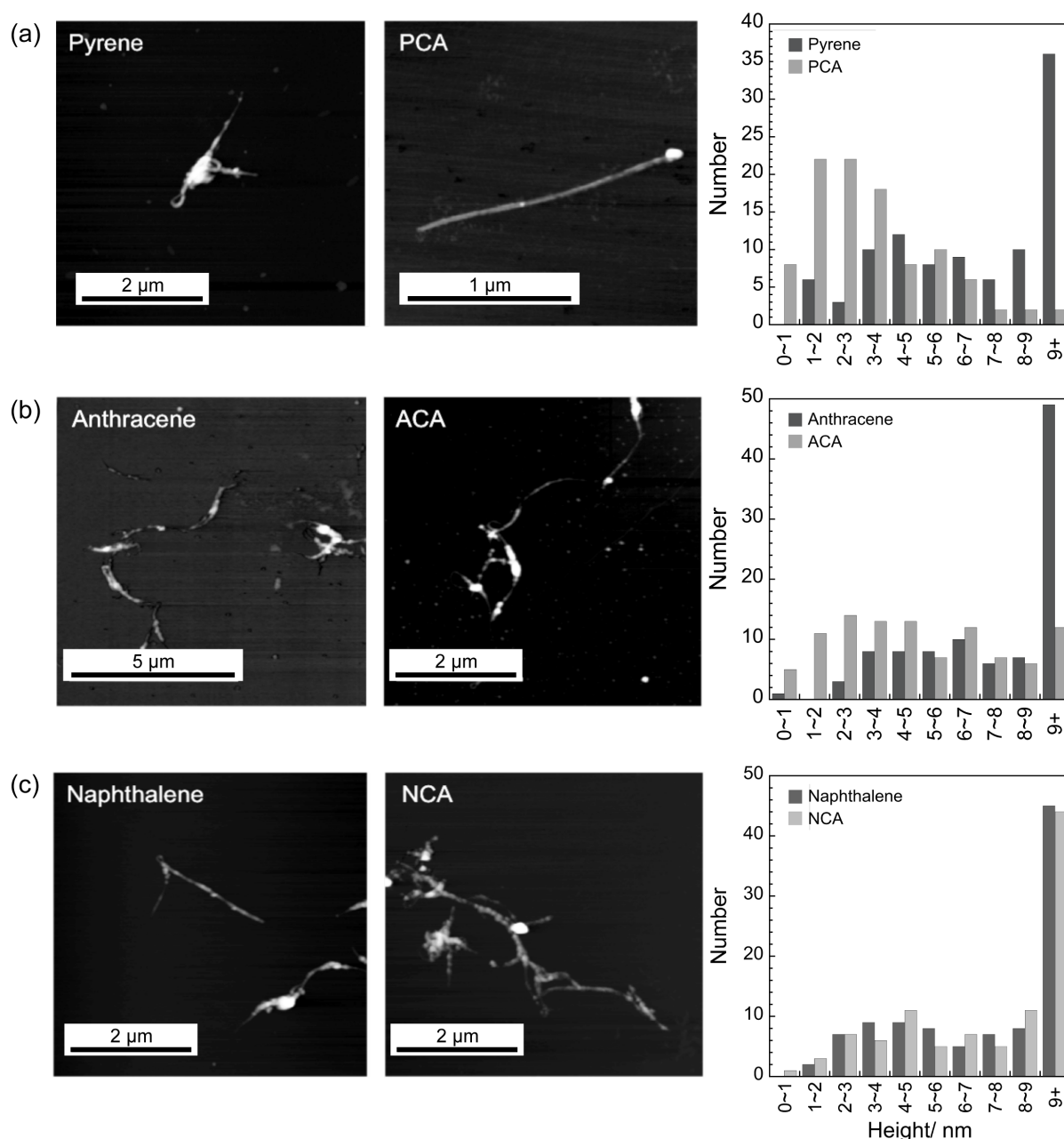


Figure 3. AFM images of (a) pyrene and PCA, (b) anthracene and ACA, and (c) naphthalene and NCA wrapped SWNTs dispersions and statistical analyses of heights of the SWNTs. Scale bars are shown in the images. In all the statistical analyses, total numbers of 100 SWNTs were analyzed.

The effects of substituted functional groups of polycyclic aromatic molecules were compared to discuss the dispersed capabilities. In case of pyrene and anthracene, the carboxylic derivatives showed higher dispersion amounts. This is possibly due to the hydrophilicity of the carboxylic derivatives. In fact, the dispersion amount of dispersed SWNTs by PCA in a buffer solution (pH 9) resulted in 2.4 times greater amounts than that in water. Therefore, the carboxylic group is considered to affect the elevation of dispersed amounts. In contrast, the dispersion amount of SWNTs by naphthalene was greater than that of SWNTs by NCA, suggesting that dispersion capabilities of simple

aromatic molecules for SWNTs could not be explained simply by the presence of substituted hydrophilic groups. Since naphthalene has the smallest aromatic ring numbers in the molecules used in this study, NCA might be too hydrophilic to interact with SWNTs.

The morphologies of the SWNTs wrapped with aromatic molecules were then investigated by AFM observation in the tapping mode using SPM9600 (Shimadzu) with a silicon cantilever (PointProbe, NCH, resonance frequency 320 kHz, force constant 42 N/m, NanoWorld) in air. The SWNTs dispersed by PCA on freshly cleaved mica surfaces were completely disentangled and isolated as shown in Figure 3a.

In contrast, when pyrene molecules were used, entangled SWNTs were observed. The heights of the SWNTs wrapped with PCA or pyrene were statistically analyzed from AFM images (Figure 3a, right). The mean height of PCA wrapped SWNTs were in a range of several nanometers, and the mean height were 3.3 nm. Since the mean height of the SWNTs were slightly greater than that of the original HiPco SWNTs, which have average diameter of 1.1 nm [17], the SWNTs wrapped with PCA were considered to be well disentangled with PCA layers on the surfaces of SWNTs. Furthermore, the mean height of PCA wrapped SWNTs was two times smaller than that of pyrene wrapped SWNTs (6.8 nm), indicating the essential roles of carboxylic groups of PCA for well disentanglement. Furthermore, since the mean heights of SWNTs wrapped with ACA and anthracene were 4.9 and 7.5 nm, respectively, it was demonstrated that the effect of carboxylic groups on disentanglement was expressed simply in the case of anthracene (Figure 3b). In contrast, the mean heights of SWNTs wrapped with NCA and naphthalene were almost the same (7.1 nm, Figure 3c); it was therefore, confirmed that aromatic ring of naphthalene was too small to interact well with the surface of SWNTs. These height values were greater than that of PCA, indicating that SWNTs wrapped with those aromatic molecules were consisted of bundled SWNTs. Therefore, it was indicated that PCA could act as good dispersants for disentanglement of bundled SWNTs, and the aromatic numbers and hydrophilic substituted groups were important for dispersion of SWNTs.

Conclusions

In conclusion, we have demonstrated that disentanglement and dispersion of SWNTs in aqueous phase can be accomplished by wrapping of several simple aromatic molecules. Quantification of dispersed amounts of aromatic molecule wrapped SWNTs by adsorption spectra indicated that PCA showed the highest dispersion capability of SWNTs as compared to other aromatic molecules used in this study. It was therefore suggested that both the interactions between the aromatic molecules and surfaces of SWNTs, and the hydrophilicity of the aromatic molecules were essential for the dispersion of SWNTs in aqueous solutions. AFM observation demonstrated that PCA wrapped SWNTs were completely disentangled from bundled SWNTs in aqueous solutions. Since PCA have simple and functionalizable chemical structures, various functions would be induced to SWNTs via PCA molecules through noncovalent interactions. Our results will contribute to basic data for construction of well-dispersed nanomaterials using SWNTs.

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Abbreviations: single-walled carbon nanotubes (SWNTs); high-pressure decomposition of carbon monoxide (HiPco); atomic force microscopy (AFM); ultraviolet-visible-near infrared (UV-Vis-NIR); 2-naphthalene carboxylic acid (NCA); 9-anthracene carboxylic acid (ACA); 1-pyrene carboxylic acid (PCA); sodium dodecylbenzenesulfonate (SDBS).