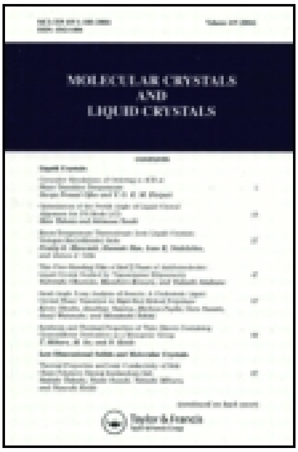

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Chirality-Dependent Changes in the Density of Single-Walled Carbon Nanotubes Oxidized by Tetrachloroaurate

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Density change of single-walled carbon nanotubes (SWCNTs) with tetrachloroaurate enables chirality sorting of the SWCNTs. In this study, we examined in detail about the density change behavior of individually solubilized (n,m)-SWCNTs caused by tetrachloroaurate using density gradients centrifugation and vis-near IR absorption spectroscopy. The (7,5)-, (8,4)- and (8,3)- SWCNTs showed a linear relationship between the density and the degree of the oxidation of the corresponding SWCNTs. Although the (6,5)-SWCNTs was hardly oxidized by tetrachloroaurate, their density increased by the addition of tetrachloroaurate.

Keywords Chirality; density gradient centrifugation; oxidation; single-walled carbon nanotubes; tetrachloroaurate

1. Introduction

Single-walled carbon nanotubes (SWCNTs) possess remarkable electronic, optical, mechanical and thermal properties that depend on the diameter and chiral angle of the constituent graphene sheets. These parameters are related to a pair of integers (n,m), the so-called chiral indices [1,2]. Although selective syntheses of SWCNTs have been reported [3], it has been difficult to synthesize a specific (n,m) species of SWCNTs. Therefore, a method for sorting of SWCNTs has been a long-awaited technique for the realization of practical applications of SWCNTs [4]. Several methods have been reported for sorting mixed SWCNTs [4,5].

The density of the SWCNTs is a typical property that depends on chirality [6]. SWCNTs with different chiralities can be separated using density gradient ultracentrifugation (DGU) [6–8]. We have already reported the density change of the SWCNTs induced by the oxidation with tetrachloroaurate ($AuCl_4^-$) leading to chirality separation [9]. In Figure 1, the overall concept of our chirality sorting method is

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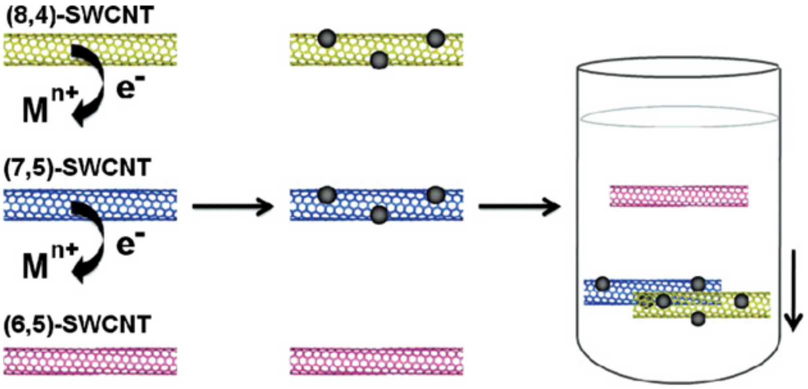

Figure 1. Representation of changes in density of the SWCNTs with metal ions. In this model, the metal generated by the reduction of a metal ion (M^{n+}) with (7,5)-SWCNT and (8,4)-SWCNT (left) adsorb on specific SWCNTs (center). This process results in the separation of (6,5)-SWCNT from (7,5)-SWCNT and (8,4)-SWCNT, which have an adsorbed metal, by DGU (right).

schematically shown. The density of the oxidized SWCNTs was sufficiently different from the unoxidized SWCNTs to allow the separation by DGU since the gold atoms or small gold clusters adsorbed on the SWCNTs resulted in the change of the density; however, the detail about this behavior is still unknown. In this work, by demonstrating the distribution of the density of the SWCNTs after the reaction with $AuCl_4^-$, we discuss the density change of the SWCNTs that depend on their chirality.

2. Experimental

SWCNTs (the so-called CoMoCat-SWCNTs, SouthWest Nanotechnologies) were dispersed in a micellar solution of sodium cholate (SC, Kishida Chemical Co., Ltd.). The experimental procedure used to obtain a solution of individually solubilized SWCNTs was the same as that reported in our previous paper [10]. An appropriate amount of an aqueous solution of $HAuCl_4$ (Wako) was mixed with the obtained SWCNT solution to give final concentrations of $AuCl_4^-$ of 0.3, 0.4, and 0.6 mM. Absorption spectra were measured in 10 min after the preparation of the mixed solutions. Iodixanol (Fresenius Kabi NorgeAS) was used for DGU (Hitachi High-Technologies Corporation) [6,9]. A SWCNT solution was layered on the top of a solution of iodixanol forming a linear density gradient. The solution was centrifuged at 41000 rpm (174000 × g) for 12 h at 22°C and 0.14 mL of each fraction was collected. The densities of the fractions were determined based on their refractive indices.

3. Results and Discussion

The formation of Au nanoparticles on the sidewalls of the SWCNTs by the direct redox reaction of $AuCl_4^-$ ions has been previously reported [11]. Figure 2 shows absorption spectra of four different SWCNT solutions in the absence or presence

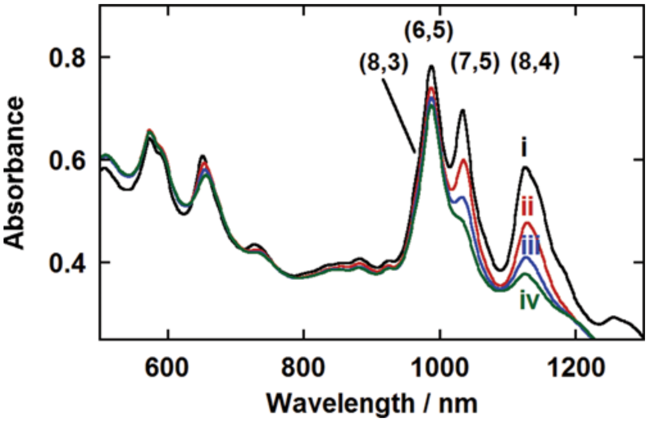

Figure 2. Absorption spectra of the SWCNTs dissolved in micellar solutions of SC in the absence and presence of $AuCl_4^-$. The concentration of $AuCl_4^-$ was i) 0, ii) 0.3, iii) 0.4, and iv) 0.6 mM.

of $AuCl_4^-$. The presence of large amounts of $AuCl_4^-$ was found to induce the decrease in the intensity of the absorption peaks at 1030, 1120, and 960 nm that correspond to the absorption of (7,5)-, (8,4)-, and (8,3)-SWCNTs, respectively. The observed intensity change is due to the oxidation of the SWCNTs by $AuCl_4^-$ [12]. Although the peak intensity at 985 nm from the (6,5)-SWCNTs slightly decreased, its degree is much smaller than those of the (7,5)-, (8,4)-, and (8,3)-SWCNTs. Difference spectra of the near-IR spectra were used to estimate the extent of non-oxidized forms of each chirality of the SWCNTs [6]. Figure 3 shows the relative extent of non-oxidized forms of the different SWCNTs plotted as a function of the concentration of $AuCl_4^-$. The relative extent of non-oxidized forms of the (8,3)-, (7,5)-, and

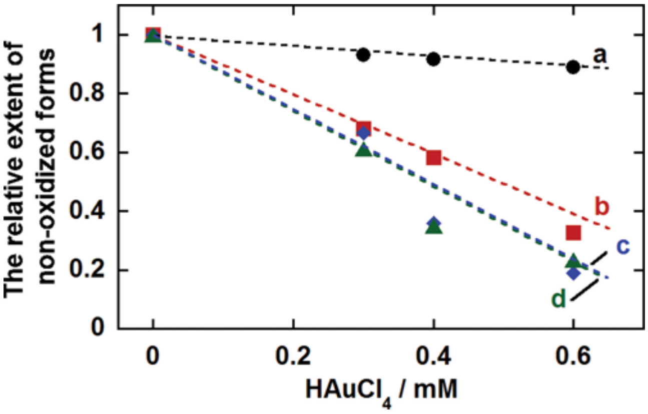

Figure 3. Relative extents of non-oxidized forms of four chiralities of the SWCNTs plotted against $AuCl_4^-$ concentrations. The chiralities of the SWCNTs were: (a) (6,5), black circles, (b) (8,3), red squares, (c) (7,5), blue diamonds and (d) (8,4), green triangles. On the vertical axis, "1" and "0" means that all of the SWCNTs were reduced or oxidized, respectively.

(8,4)-SWCNTs were found to decrease as the increase in the concentration of $AuCl_4^-$. In sharp contrast, the extent of non-oxidized (6,5)-SWCNTs did not depend on the concentration of $AuCl_4^-$, indicating that the oxidation of the (6,5)-SWCNTs hardly occurred in the presence of $AuCl_4^-$. This behavior would be derived from the positive redox potential of the (6,5)-SWCNTs (0.64 V vs SCE) compared to the those of the (8,3)-, (7,5), and (8,4)-SWCNTs (0.59, 0.54, and 0.52 V vs SCE) [11]. The standard redox potential of the $Au/AuCl_4^-$ is 0.80 V vs SCE. This result is consistent with that of the oxidation of the SWCNTs using photoluminescence measurements [9].

Four different SWCNT solutions in the absence or presence of $AuCl_4^-$ were used for DGU measurements and their densities were determined. It was found that during the 12-h DGU procedure, the intensities of the absorption peaks at 1030, 1120, and 960 nm gradually recovered. It means that the observed absorption after the DGU procedure is from the SWCNTs existed in the solutions. In Figure 4, the photographs of the vials of the SWCNT solutions (A, D, G, and J), and absorption spectra of the collected fractions (B, E, H, and K) are shown. Using these spectra, the concentrations of the SWCNTs of all fractions were evaluated in the same manner as in Figure 3, in which each concentration was normalized to the value of the (7,5)-SWCNTs obtained in the absence of $AuCl_4^-$, which was obtained from Figure 4 (B) (green line). In Figure 4 (C, F, I, and L), the normalized concentration of each chirality of the SWCNTs is plotted against the density of the fractions. These plots reveal the density profiles of the four chiralities of the SWCNTs before and

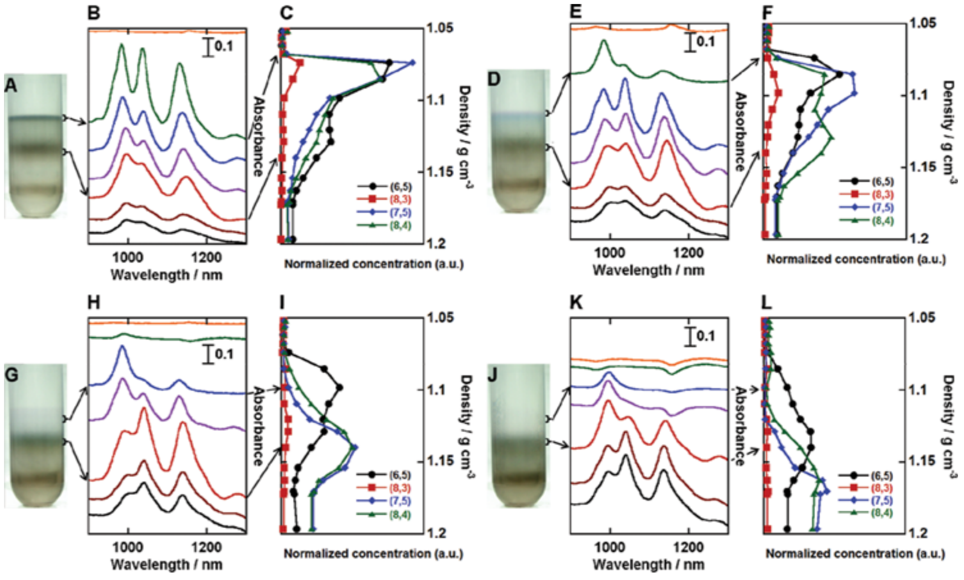

Figure 4. Photographs (A, D, G, and J) of vials of SWCNT solutions after DGU, absorption spectra (B, E, H, and K) of the collected fractions, and normalized SWCNT concentrations plotted against solution density (C, F, I, and L) in the absence (A) and presence (D, G and J) of $AuCl_4^-$. The concentrations of $AuCl_4^-$ were: A) 0, D) 0.3, G) 0.4, and J) 0.6 mM. The densities of the collected fractions in B, E, H and K were 1.06 (orange), 1.07 (green), 1.1 (blue), 1.12 (purple), 1.14 (red), 1.16 (brown), and 1.17 g/cm^3 (black). The chiralities of the SWCNTs plotted in C, F, I, and L were (6,5) (black circles), (8,3) (red squares), (7,5) (blue diamonds), and (8,4) (green triangles).

after the oxidation with $AuCl_4^-$. In the absence of $AuCl_4^-$, the absorption spectrum of the fraction with a density of 1.07 g/cm^3 ((column B), green line) shows three peaks and one shoulder that is typical of the isolated SWCNTs. In the presence of $AuCl_4^-$ (D-L), the SWCNTs appeared at the bottom of the tubes, indicating that the densities of the SWCNTs increased upon the addition of $AuCl_4^-$. The density profiles (F, I, and L) indicated that the densities of the SWCNTs increased by the addition of $AuCl_4^-$. For example, in the presence of 0.4 mM $AuCl_4^-$ (I), the peaks in the density profiles of the SWCNTs were 1.10 g/cm^3 for (6,5)- and 1.17 g/cm^3 for (8,4)- and (7,5)-SWCNTs. In the solution containing 0.6 mM $AuCl_4^-$, the density profile of the (6,5)-SWCNTs exhibited a peak at 1.13 g/cm^3. The changes in density of (6,5)-SWCNTs were observed but smaller than those of the other SWCNTs.

To discuss the relation between the change in the density of the SWCNTs and their oxidation behavior, the typical densities of the four SWCNTs taken from Figure 4 are plotted against the relative extent of non-oxidized forms of the SWCNTs in Figure 5. Here, the typical densities were determined from the positions of the peaks in the density profiles in Figure 4C, F, I, and L. In the case of the (6,5)-SWCNTs, the typical density changed from 1.06 to 1.13 g/cm^3 without significant changes in the relative extent of non-oxidized forms (filled circles). In contrast, the three other chiralities of the SWCNTs showed linear relation between the density and the degree of the oxidation; when the relative extent of non-oxidized forms changed from 1 to 0.2, the density changed from 1.06 to 1.17 g/cm^3. This strongly suggests that $AuCl_4^-$, which should be reduced to form gold atoms or small gold clusters [9], adsorbed on the surface of the SWCNTs, leading to the increase in their density. Although $AuCl_4^-$ did not efficiently oxidize the (6,5)-SWCNTs [9], the density of the SWCNTs increased significantly upon the addition of $AuCl_4^-$. In other words, $AuCl_4^-$ changed the density of the (6,5)-SWCNTs without oxidation. the mechanism for the density change for (6,5)-SWCNTs is under investigation.

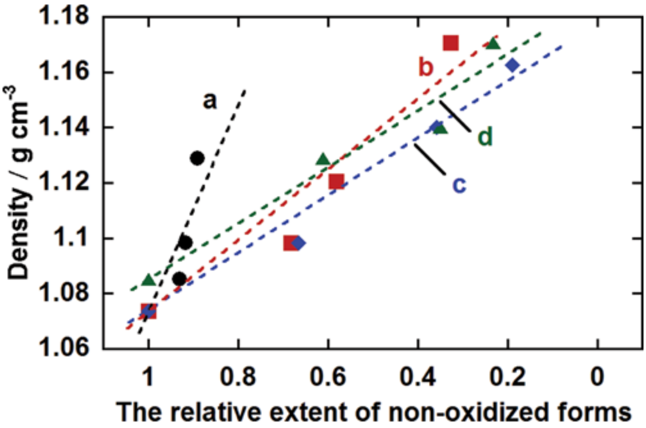

Figure 5. Densities of the SWCNTs plotted against the relative extents of non-oxidized forms of the SWCNTs. The chiralities of the SWCNTs were (a) (6,5), black circles, (b) (8,3), red squares, (c) (7,5), blue diamonds, and (d) (8,4) green triangles. Densities were determined from the positions of the peaks in the density profiles shown in Figure 4 (C, F, I, and L). The relative extents of non-oxidized forms were obtained from Figure 3.

4. Conclusion

In summary, we examined the behavior of the changes in density of individually dissolved (n,m)-SWCNTs induced by the addition of $AuCl_4^-$. DGU and absorption spectroscopy revealed that the (7,5)-, (8,4)- and (8,3)-SWCNTs showed linear relationship between the density and the degree of oxidation of the corresponding SWCNTs. These linear relation and chirality dependence indicate that $AuCl_4^-$ are reduced to form gold atoms or clusters adsorbed on the surfaces of the SWCNTs, leading to the increase in their density. However, no such behavior was observed for the (6,5)-SWCNTs. This is due the difference in the redox potentials of these nanotubes as discussed. The present method is useful in fundamental understanding of chirality-dependent density change in the (n,m)-SWCNTs induced by the adsorption of metal nanoparticles generated by the redox reactions with the tubes.

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