Carbon Nanotubes

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Efficient Separation of (6,5) Single-Walled Carbon Nanotubes Using a "Nanometal Sinker"**

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Single-walled carbon nanotubes (SWNTs) are one-dimensional conducting nanosized molecular wires that possess remarkable electrical, mechanical, thermal, and optical properties.[1,2] Although selective syntheses and the subsequent separation of SWNTs have been reported,[3] the general difficulties in synthesizing SWNTs of a specific chirality means that SWNT chirality sorting has been a long-awaited technique for the realization of practical applications of SWNTs. These compounds may be especially useful in the field of nanoelectronic devices since the properties of the SWNTs depend on their size and electronic structures.[4,5] Zheng and co-workers[6–8] reported the separation of (6,5)- and (9,1)- enriched SWNTs from a sample of SWNTs dissolved in an aqueous solution of oligo single-stranded DNA $(GT)_{30}$ by using size-exclusion chromatography (SEC). Dai and co-workers[5] have described the separation of SWNTs with a small range of (not single) chiralities using SEC for oligo-single-stranded DNA-wrapped SWNTs. Recently, some fluorine-based polymers have been found to selectively dissolve semiconducting SWNTs.[9,10] Papadimitrakopoulos and co-workers reported that helical assemblies of flavin mononucleotide dissolve SWNTs, and have succeeded in the isolation of samples with an 85% chirality enrichment of (8,6) SWNTs using the chirality-dependent affinity of the dissolved SWNTs.[11] Hersam and co-workers reported that the density-gradient ultracentrifugation (DGU) technique is powerful enough to separate SWNTs of different diameters.[12,13] Strano and co-workers described the separation of covalently functionalized and nonfunctionalized SWNTs by using the difference in their densities, although the fine sorting of SWNTs that have very similar diameters was difficult.[14]

Herein, we present a novel strategy toward SWNT chirality sorting; that is, a method that uses "nanometal sinkers" that adsorb onto specific SWNTs. The resulting nanometal-sinker-adsorbed SWNTs can be separated from other SWNTs by DGU (Figure 1). SWNTs have their own electronic states that depend on their electronic structures,

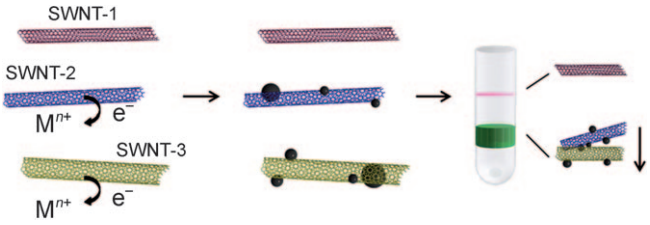

Figure 1. Representation of the concept of SWNT chirality sorting or "chirality fishing". In this model, the "nano-metal sinkers" generated by the reduction of a metal ion (M^{n+}) with SWNT-2 and SWNT-3 (left) adsorb on specific SWNTs (center). This process results in the separation of SWNT-1 from SWNT-2 and SWNT-3, which have an adsorbed nano-metal sinker, by DGU (right).

which are represented as chirality indices (n,m). We have taken advantage of this fundamental property of the SWNTs for their sorting; the overall concept is shown in Figure 1. Electron transfer from SWNT-2 and SWNT-3 to the metal ions results in the formation of the nanometals on the surfaces of the SWNTs. However, for SWNT-1, no such electron transfer occurs because of the difference in the electronic states. As a result, the difference in weight between these species leads to the separation of the SWNTs-1 from the other SWNTs.

As-produced SWNTs (CNI) were dispersed in an aqueous solution (pH 7.5, phosphate buffer) of sodium cholate (SC) by sonication using a bath-type sonicator for 1 hour.[15] $AuCl_4^-$ ions were then added to the supernatant solution (see the Supporting Information for experimental procedures). The buffer solution was used in order to avoid the effect of buoyant density and to control the redox reaction of the $AuCl_4^-$ ions. The resulting solution was centrifuged for 1 h at 25 °C, and the upper 80% of the supernatant was collected.[15]

The formation of Au nanoparticles on the sidewalls of the SWNTs by the direct redox reaction of $AuCl_4^-$ ions has been previously reported.[16,17] We found that the addition of $AuCl_4^-$ ions to the SWNTs dissolved in an aqueous micelle of SC caused an absorbance decrease in the near-infrared (NIR) spectra of the SWNTs. This decrease arises from the electron-transfer reaction between the SWNTs and $AuCl_4^-$ ions (Figure 2).[18–20] NIR photoluminescence (PL) spectra of these solutions are shown in Figure 3, and show PL quenching as the amount of $AuCl_4^-$ ions is increased. Interestingly, the strong PL of the (6,5) SWNTs as well as a weak PL from the

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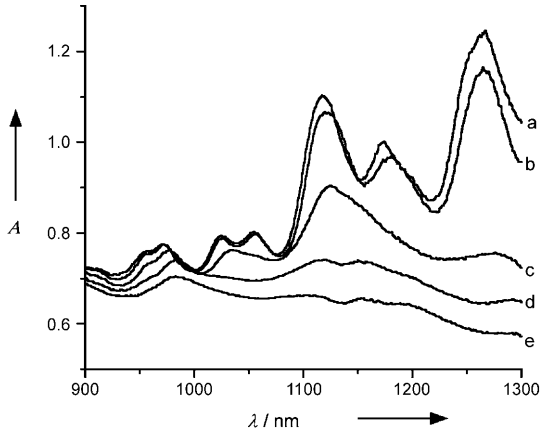

Figure 2. NIR absorption spectra of the SWNTs dissolved in aqueous micellar solutions of SC before and after the addition of $AuCl_4^-$ ions. The concentrations of $AuCl_4^-$ ions are: a) 0, b) 0.2, c) 0.4, d) 0.8, and e) 1.6 mM.

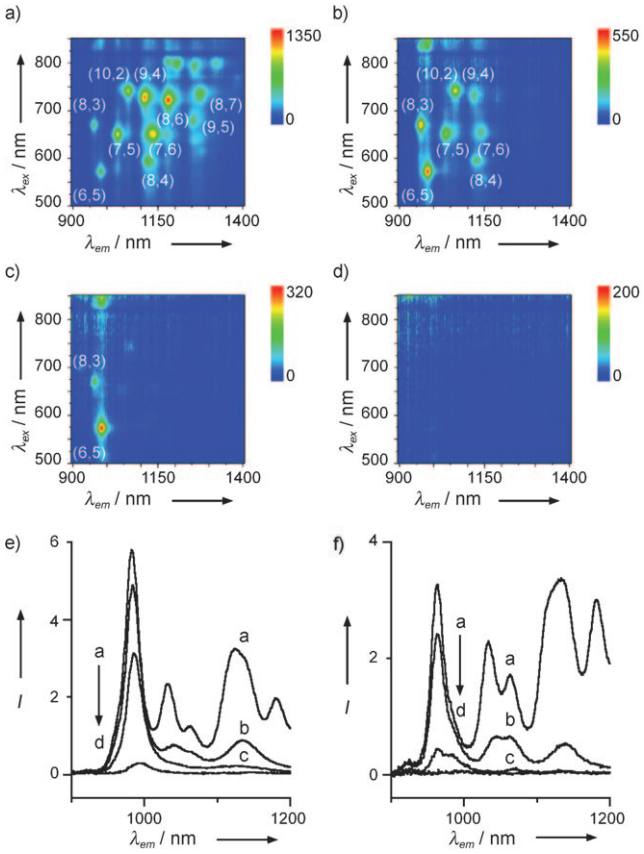

Figure 3. 2D-PL mapping of the SWNTs dissolved in aqueous SC micellar solutions in the presence of a) 0, b) 0.4, c) 0.8, and d) 1.6 mM $AuCl_4^-$ ions. NIR PL spectra of the SWNT solutions in (a–d). e) Excitation at 575 nm and f) excitation at 680 nm.

(8,3) SWNTs still remained after the addition of $AuCl_4^-$ ions (Figure 3e), which indicates that the oxidation of (6,5) and (8,3) SWNTs with $AuCl_4^-$ ions is more difficult than that of the other SWNTs. It is evident that the reaction is chirality-selective; that is, the SWNTs with diameters greater than 0.8 nm with absorbances between 1000–1300 nm were preferentially oxidized by $AuCl_4^-$ ions. As shown in Figure 3a,b, when the concentration of $HAuCl_4$ was 0.8 mM, the degree of quenching of the (8,3) SWNTs was greater than that of the (6,5) SWNTs. Based on these results, we explored the possibility of our "SWNT chirality fishing" concept.

DGU was carried out using iodixanol for individually dissolved SWNTs in aqueous micelle solutions of SC with and without (control experiment) $AuCl_4^-$ (0.8 mM). Density gradients were created in centrifuge tubes by layering and subsequent diffusion. The SWNT solution was layered on the top of the gradient, and centrifuged for 8 h at 174000 g (see the Supporting Information). Figure 4 shows photographs and two-dimensional PL mapping after DGU of the SWNT samples in the presence (left-hand column) and absence (right-hand column, control) of $AuCl_4^-$ ions. The $AuCl_4^-$-treated SWNT solution appears as a broad band in the lower position of the tube (Figure 4a); this effect is not observed for the control sample (Figure 4e), thus indicating that the density of the $AuCl_4^-$-treated SWNTs is higher than that of the control sample. These results suggest that the $AuCl_4^-$ ions

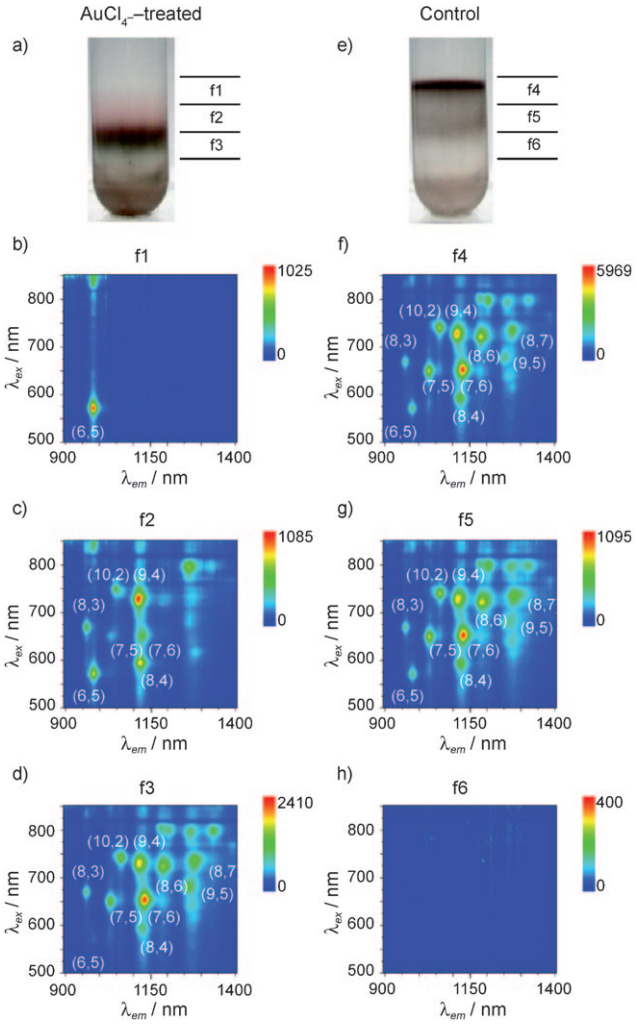

Figure 4. a,e) Photographs of DGU tubes. 2D mapping of the PL spectra of the SWNT solutions from bands b) f1, c) f2, d) f3, e) f4, g) f5, h) f6. Left-hand column: an $AuCl_4^-$-treated SWNT solution; right-hand column: control sample without $AuCl_4^-$ ions.

reacted with SWNTs to form Au^0, which acted as the "sinker", on the surfaces of the SWNTs. In fact, X-ray photoelectron spectroscopy (XPS) of the sample from band f3 revealed the presence of metallic gold (see Figure S1 in the Supporting Information). As can be seen in Figure 4c,d, the two-dimensional PL patterns of the solutions from bands f2 and f3 show the existence of many SWNT chiralities, which is also seen in bands f4 and f5 in the control samples (Figure 4f,g). The most important result is seen in Figure 4b, which shows the PL from f1. Only one PL spot, which has the chirality index of (6,5) SWNTs, is visible in this image. In contrast, no PL spot was seen from the solution from band f6 (control).

The absorption spectra of the solution from band f1 and of the non-$AuCl_4^-$-treated SWNT sample show a sharp S11 peak (the first semiconducting peak; red line) at 976 nm in the solution of band f1 (Figure 5a). This peak arises from the (6,5) SWNTs, and is in sharp contrast to the control spectrum of the SWNTs, in which many peaks that arise from the SWNTs with many different chirality indices, appeared in the visible and NIR regions (black line). Figure 5b shows the surface plot of PL intensity of the solution from band f1, in which the peak that corresponds to the (6,5) SWNTs is essentially the only component. Thus, the combination of the oxidation by $AuCl_4^-$ ions followed by the DGU treatment realized the chirality separation of the (6,5) SWNTs from other SWNTs in the solution.

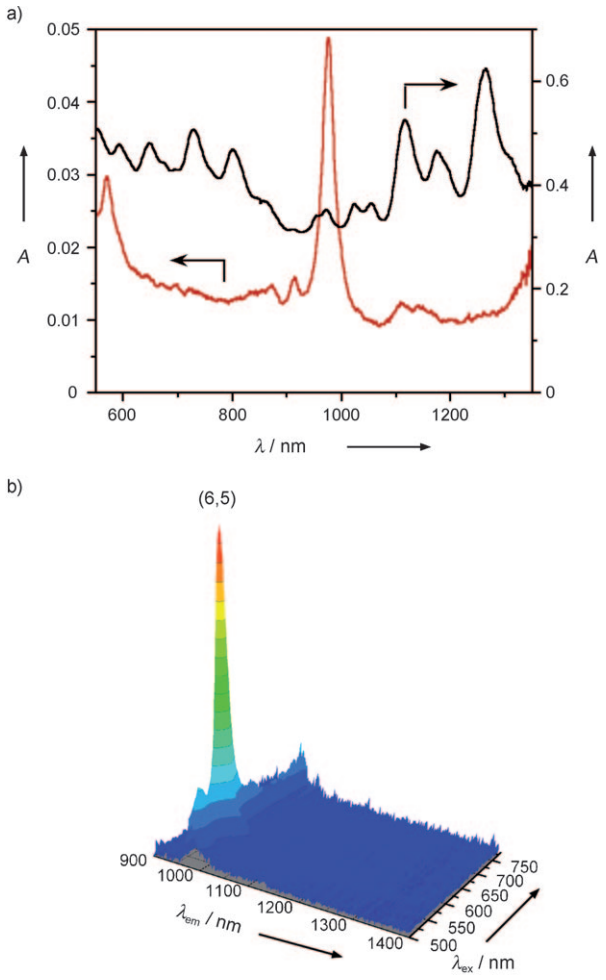

Figure 5. a) Vis/NIR absorption spectra of SWNT solutions taken from band f1 of the DGU tube (red) and from the non-$AuCl_4^-$-treated SWNTs (black). b) Surface plot of PL intensity as a function of emission and excitation wavelengths of the SWNT solution taken from band f1 (red curve in (a)).

It must be noted that the (8,3) SWNTs are not retained in the f1 band. In general, the separation of the SWNTs such as (6,5) SWNTs (0.757 nm) and (8,3) SWNTs (0.782 nm) is difficult as their diameters are very similar. In fact, these two different SWNTs cannot be adequately separated by simple DGU.[13] In sharp contrast, in our approach, (8,3) SWNTs reacted with $AuCl_4^-$ ions, as confirmed by the spectral bleach in the absorption spectrum of the (8,3) SWNTs after the addition of $AuCl_4^-$ ions. This reaction resulted in the formation of $Au^{(0)}$ on the surface of the nanotubes. No such reaction was observed for the (6,5) SWNTs. The experimental result is explained by the difference in the electronic states of the (8,3) and (6,5) SWNTs,[21] in that the oxidation potential of the (8,3) SWNTs is lower than that of the (6,5) SWNTs. Therefore, the separation of these two different SWNTs by using the DGU method is possible since the (8,3) SWNTs/Au^0 are heavier than the (6,5) SWNTs. As the PL intensity of the (6,5) SWNTs after the DGU was approximately half that before the DGU, it can be inferred that the present method is efficient for the sorting of the (6,5) SWNTs. When we used ultracentrifugation (120000 g) instead of DGU, the separation of the (6,5) SWNTs from the other SWNTs was not successful (see Figure S2 in the Supporting Information).

In conclusion, we have succeeded in the separation of (6,5) SWNTs from the other SWNTs in a sample of HiPCo SWNTs. We emphasize that our method is powerful enough to separate SWNTs that have very similar diameters and cannot be separated by using simple DGU. The sorting relies on differences in the oxidation potential of the various SWNTs and thereby spares tubes with the highest oxidation potential and the lowest reaction rate. Therefore, it is not possible at present to isolate desired specific (*n*,*m*)-SWNTs. Sophisticated further material design to realize the selective reactions of SWNTs (see Figure S3 in the Supporting Information) could ultimately allow the separation of SWNTs based on their chirality.

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