NANO LETTERS

Letter

pubs.acs.org/NanoLett

Optical Isomer Separation of Single-Chirality Carbon Nanotubes Using Gel Column Chromatography

Huaping Liu,[†,‡] Takeshi Tanaka,[§] and Hiromichi Kataura*[,§,⊥]

[†]Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

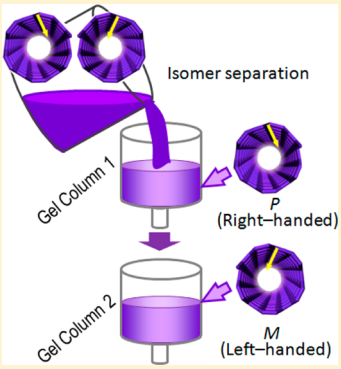
[‡]Collaborative Innovation Center of Quantum Matter, Beijing 100190, China

[§]Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8562, Japan

[⊥]Japan Science and Technology Agency, CREST, Kawaguchi, Saitama 330-0012, Japan

Supporting Information

ABSTRACT: We report a gel column chromatography method for easily separating the optical isomers (i.e., left- and right-handed structures) of single-chirality carbon nanotubes. This method uses the difference in the interactions of the two isomers of a chiral single-wall carbon nanotube (SWCNT) with an allyl dextran-based gel, which result from the selective interaction of the chiral moieties of the gel with the isomers. Using this technique, we sorted optical isomers of nine distinct (n, m) single-chirality species from HiPco SWCNTs, which is the maximum number of isolable species of SWCNTs reported to date. Because of its advantages of technical simplicity, low cost, and high efficiency, gel column chromatography allows researchers to prepare macroscopic ensembles of single-structure SWCNTs and enables the complete discovery of intrinsic properties of SWCNTs and advances their application.



KEYWORDS: *Carbon nanotubes, Optical isomers, Bulk separation, Gel chromatography*

A small difference in atomic arrangements among single-wall carbon nanotubes (SWCNTs) causes striking differences in their optical and electronic properties.[1] The bulk production of single-structure SWCNTs with identical properties is paramount for studies of their intrinsic properties and technological applications in the fields of optics, electronics, and optoelectronics. To achieve this objective, numerous scientists have been pursuing single-structure control of SWCNTs on a large scale since their discovery 20 years ago. Until recently, several techniques have allowed researchers to prepare single-chirality SWCNTs with diameters less than 1.2 nm[2−7] or even their macroscopic ensembles,[8,9] which accelerates the applications of SWCNTs in optoelectronic device.[10−12] However, each chiral SWCNT has a pair of left- and right-handed structures.[13,14] They exhibit different optical activities[15,16] and are named here as optical isomers. Producing populations of single-isomer species is the ultimate step for obtaining true single-structure SWCNTs and, thus, is critical to truly unlock their intrinsic properties and advance their applications.

The properties of a SWCNT can be effectively translated into their macroscopic-ordered materials such as single-crystals of SWCNTs. The scalable production of single-isomer species is an essential prerequisite for the fabrication of chiral single-crystals of SWCNTs with various band-gaps. They are brand new three-dimensional materials which scientists dream of achieving because they could lead to the discovery of novel physical properties and applications. Many obscured and convoluted features such as the chiral optical response and structure-dependent lengths of C−C bonds of SWCNTs can be resolved, which is very difficult to achieve using a mixture or individual SWCNTs. The fabrication of chiral single-crystals of SWCNTs could also open broad avenues for the application in optical components, biological sensors, production of chiral light, and asymmetric autocatalysis.[17−20] The discovery of novel properties and advancing applications of SWCNTs drives scientists to achieve macroscopic ensembles of single-isomer species.

Recently, several groups performed optical isomer separation of SWCNTs using the synthesized chiral organic molecules as isomer selectors,[16,21−26] but only a complicated isomer mixture of many different chiral SWCNTs was achieved. Moreover, the separation yield was insufficient because of the limited production and high cost of the synthetic chiral molecules. The density gradient ultracentrifugation (DGU) technique was also developed to separate isomers of near single-chirality (n, m) SWCNTs using chiral sodium cholate as a surfactant.[6,27] However, the DGU method is complex and requires a long separation process. The separated species contain a density medium, such as iodixanol, which is very expensive and remains

Received: July 8, 2014
Revised: October 16, 2014
Published: October 27, 2014

dx.doi.org/10.1021/nl5025613 | *Nano Lett.* 2014, 14, 6237−6243

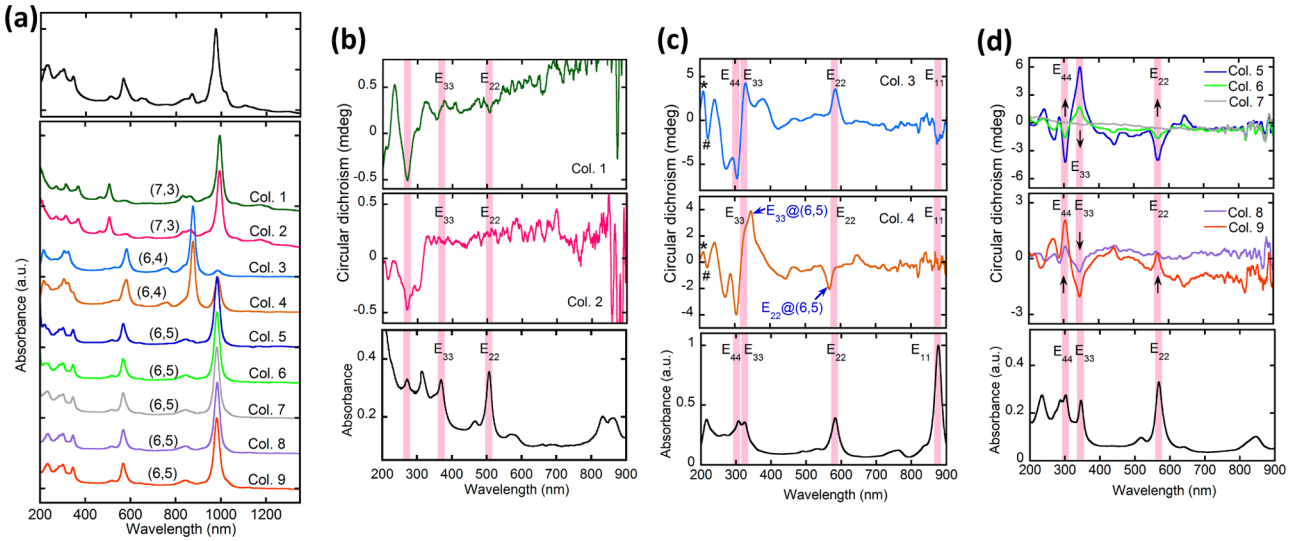


Figure 1. Separation and characterization of optical isomers of single-chirality carbon nanotubes. (a) Optical absorption spectra of the separated (*n*, *m*) fractions from the Column 1 semiconducting fraction in the first separation. The top panel corresponds to the Column 1 fraction in the first separation. The lower panel presents the normalized spectra of the corresponding (*n*, *m*) fractions separated in the second separation. The original spectra are presented in Figure S4 (Supporting Information). (b)−(d) CD spectra for the fractions of (7, 3), (6, 4), and (6, 5) nanotubes in (a). The lowest panels in (b)−(d) present the UV−vis absorbance spectra of the corresponding nanotubes. In (c), the positive * peak at 207 nm and negative # peak at 220 nm indicate the CD signals of (*M*)-(6, 4) isomers in the UV region. Col. = Column.

as an impurity after separation. In addition, the use of chiral molecules in the aforementioned methods affects the characterization of the separated optical isomers and thus affects any evaluation of their purity. These disadvantages preclude the large-scale production and practical applications of single-isomer species. A novel, low-cost, and bulk separation technique that avoids the use of chiral dispersants is highly desirable for sorting single-isomer species.

In the present work, we report a simple, low-cost, and highly efficient method for the optical isomer separation of single-chirality SWCNTs using gel column chromatography. We achieved the optical isomer separation of nine distinct (*n*, *m*) single-chirality SWCNTs including (7, 3), (6, 4), (6, 5) (7, 5), (7, 6), (8, 4), (9, 4), (8, 6), and (8, 7), which is the maximum number of isolable species of SWCNTs reported to date. Among them, the optical isomer separation of (7, 6), (9, 4), (8, 6), and (8, 7) sing-chirality species was first reported. This technique overcomes all the disadvantages of the aforementioned methods, allows researchers to separate optical isomers of single-chirality species on a large scale, and enables the single-crystal preparation of carbon nanotubes.

We recently developed a gel column chromatography method for the chirality separation of SWCNTs based on the different interaction strengths of distinct (*n*, *m*) SWCNTs with Sephacryl gel (Sephacryl S-200HR, GE Healthcare, Little Chalfont, U.K.).[8] Simply injecting an excess amount of SWCNT dispersion into multistage gel columns leads to the sorting of SWCNTs across different columns based on chirality. Using this technique, we achieved 13 (*n*, *m*) single-chirality species. Sephacryl gel is a composite gel prepared through covalent cross-linking of allyl dextran with *N*,*N*′-methylene bis(acrylamide) (see Supporting Information, Figure S1). Several papers have reported that dextran and its derivatives provide very good recognition of chiral molecules and can be used as chiral selectors for the enantiomer separation of various drugs.[28−31] According to this finding, we expected that Sephacryl gel would exhibit selectivity in its interaction with the optical isomers (i.e., left- and right-handed structures) of chiral SWCNTs; thus, the isomer separation of single-chirality SWCNTs could be achieved using the gel chromatography technique.

To clarify our hypothesis, we applied gel column chromatography to the isomer separation of SWCNTs. The experimental procedure was the same as that used for single-chirality separation of SWCNTs[8] (see Supporting Information, Experimental Section). A SWCNT dispersion was prepared by sonicating SWCNTs (HiPco, RØ 500, 1.0 ± 0.3 nm, NanoIntegris Inc., Montreal, Canada) in an aqueous solution of 2 wt % sodium dodecyl sulfate (SDS). Several gel columns were connected end-to-end to form multistage columns. Before being connected, each column was packed with 1.4 mL of gel beads (Sephacryl S-200HR). After the gel columns were equilibrated with 2 wt % SDS solution, an excess amount (5 mL) of SWCNT dispersion (0.15 mg mL^{-1}) was applied to the column series. The semiconducting SWCNTs were separated by chirality across the different columns (Supporting Information, Figures S2a and S3); however, each sorted fraction contained a mixture of various species.[8] To achieve the simultaneous separation of single-chirality SWCNTs and their optical isomers, each semiconducting fraction was separated repeatedly using the above separation process (Supporting Information, Figure S2b). In this step, the quantity of the semiconducting dispersion loaded sufficiently large that the optical isomers of the same single-chirality species were able to be sorted across the different gel columns. In a typical experiment, 10-ml aliquots of the semiconducting fraction (16 $\mu g\ mL^{-1}$) were applied to the gel column series. The adsorbed nanotubes in the gel column were desorbed with an aqueous solution of 5 wt % SDS.

After a second separation of the Column 1 semiconducting fraction in the first separation run, we sorted high-purity (7, 3) into two columns, (6, 4) SWCNTs into two gel columns, and (6, 5) SWCNTs across five gel columns, as illustrated in Figure 1a (also see Figure S4, Supporting Information). The optical

dx.doi.org/10.1021/nl5025613 | *Nano Lett.* 2014, 14, 6237−6243

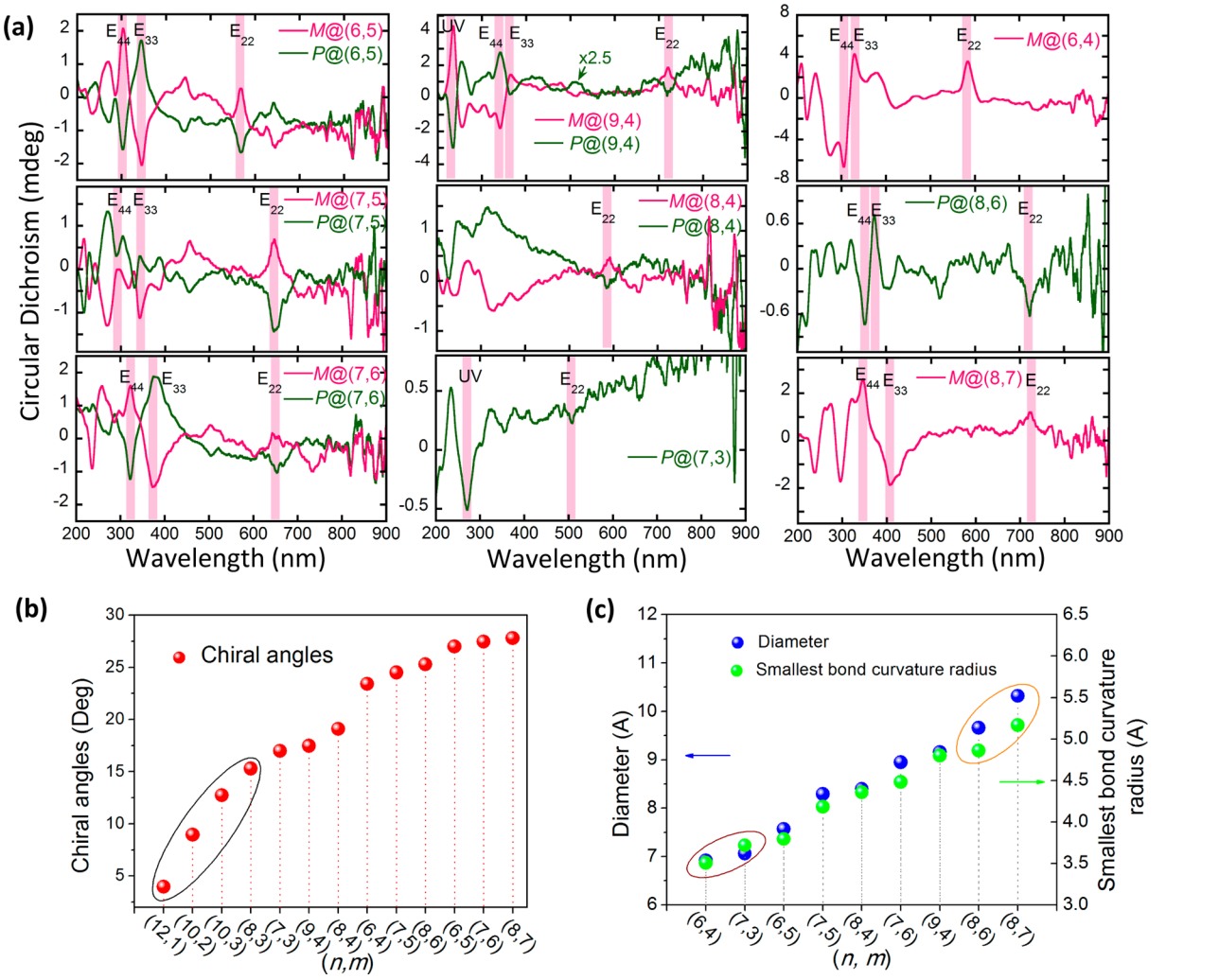


Figure 2. Characterization of the sorted isomers of nine distinct (*n*, *m*) single-chirality species. (a) CD spectra. The corresponding optical absorption spectra are shown in Figures S5−S6 (Supporting Information). (b) Comparison of the chiral angles. The optical isomers of the (*n*, *m*) species inside the circle are not separated. (c) Comparison of the diameters and smallest C−C bond curvature radii. For the (*n*, *m*) nanotubes inside two circles, only one of their two optical isomers was sorted.

isomers of SWCNTs exhibit circular dichroism (CD),[15,16] which can be tuned as a function of their atomic structures.[14,32] To confirm whether the optical isomers of the (*n*, *m*) nanotubes were separated, we characterized the nanotubes using a CD spectrometer. Figure 1b−d present the CD spectra for the sorted (7, 3), (6, 4), and (6, 5) fractions. Their unambiguous CD spectra strongly demonstrate that the optical isomer separation of these single-chirality nanotubes has been achieved. In Figure 1b, the (7, 3) fractions exhibit weak (Column 1) or no CD peaks (Column 2) at the E_{22} and E_{33} transition wavelengths but strong CD signals in the UV absorbance region. This result indicates that the (7, 3) fractions are slightly enriched in one of their optical isomers. The CD spectrum (Figure 1c) for the first (6, 4) fraction (Column 3) exhibits strong CD signals at the E_{22} and E_{33} transition wavelengths, and even a weak CD peak at the E_{11} can be detected, indicating that this fraction is highly enriched with one of the nanotubes' optical isomers. However, the second (6, 4) fraction (Column 4) exhibits the CD signals of (6, 5) nanotubes at the E_{22} and E_{33} peak positions instead of (6, 4) nanotubes, although CD peaks, such as the positive peak at 207 nm and negative peak at 220 nm for (6, 4) nanotubes in UV region, are still present. This result suggests that the minority (6, 5) nanotubes in the second (6, 4) fraction are highly enriched with one of their optical isomers. In the case of the sorted (6, 5) fractions (Columns 5−9) in Figure 1d, the CD spectra at the E_{22} and E_{33} transition wavelengths clearly undergo the changes from negative to positive and from positive to negative. Similar changes of the CD signals in the UV region are also observed. These results sufficiently demonstrate that both optical isomers (left- and right-handed structures) of the (6, 5) nanotubes have been achieved. On the basis of results previously reported by Peng et al.,[21,22] the SWCNTs exhibiting a positive E_{22} transition CD peak were identified as left-handed isomers and denoted (*M*) according to the IUPAC nomenclature,[33] whereas the SWCNTs with a negative E_{22} transition CD peak were identified as right-handed isomers and denoted (*P*). On the basis of the results in Figure 1d, we can conclude that the (*P*)-(6, 5) nanotubes exhibit stronger interaction with the gel than their corresponding (*M*) structures.

To separate additional optical isomers of single-chirality SWCNTs, we performed a second separation of the remaining different semiconducting fractions collected in the first

dx.doi.org/10.1021/nl5025613 | *Nano Lett.* 2014, 14, 6237−6243

Table 1. Highest relative purities of the (M)/(P)-isomers separated by gel column chromatography

(n, m)		(6, 4)		(7, 3)		(6, 5)		(7, 5)		(8, 4)		(7, 6)		(9, 4)		(8, 6)		(8, 7)	
isomers		M	P	M	P	M	P	M	P	M	P	M	P	M	P	M	P	M	P
relative purity (mdeg)	two-step methods	6.6		−0.4		2.3	−9.8	6.3	−3.7	3.7	−0.7	1.0	−1.6	11.8	−4.2		−3.9	0.5	
	temperature control	11.0					−6.6	6.9	−2.4	5.9			−6.2				−3.6		

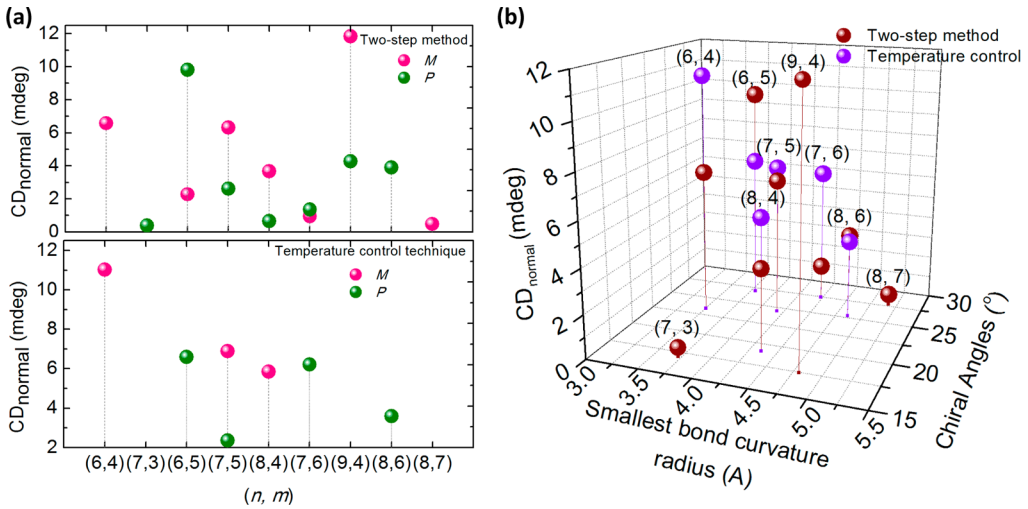


Figure 3. Highest relative optical purity distribution of the isomers separated using the two-step method and temperature control technique. (a) Comparison of the highest optical purities for the (*M*)- and (*P*)-isomers separated using the two-step method and temperature-control technique. (b) Highest optical purities of the separated isomers as a function of their diameters and chiral angles.

separation using the previously described method. The isomers of another six distinct (*n, m*) single-chirality SWCNTs has been achieved, as illustrated in Figures S5−S6 (Supporting Information). Finally, we separated the optical isomers of nine distinct (*n, m*) single-chirality SWCNTs from raw HiPco SWCNTs, including (7, 3), (6, 4), (6, 5) (7, 5), (7, 6), (8, 4), (9, 4), (8, 6), and (8, 7) SWCNTs, as shown in Figure 2a. As reported previously,[8] we were able to separate 13 (*n, m*) single-chirality SWCNTs using the two-step gel chromatography. However, the CD spectra of the remaining four single species of (8, 3), (10, 2), (10, 3), and (12, 1) did not exhibit clear CD features. Small chiral angles are the common feature of these four species, (Figure 2b), suggesting that Sephacryl gel likely exhibit less recognition of the optical isomers of the nanotubes with smaller chiral angles. In addition, for the (7, 3) and (6, 4) nanotubes with smaller diameters/C−C bond curvature radii and (8, 6) and (8, 7) nanotubes with larger diameters/C−C bond curvature radii (Figure 2c), although they have larger chiral angles, only one of their optical isomers was separated (Figure 2a). The diameters/C−C bond curvatures of SWCNTs are possibly another important factor that affects the optical isomer separation. Furthermore, unlike the (6, 5) nanotubes, the (*M*)-isomers for the (7, 5), (8, 4), (9, 4) nanotubes exhibit stronger interaction with the gel than their corresponding (*P*)-structures on the basis of their adsorption order on the gel. This finding indicates that the gel has no consistent affinity for a particular handedness for all chiral SWCNTs. Recently, we developed temperature-controlled gel chromatography for the one-step separation of single-chirality SWCNTs,[34] which has also been demonstrated to be able to separate the optical isomers of single-chirality SWCNTs (Supporting Information, Figure S7), enabling the industrial separation of the optical isomers.

The purity of the separated isomers is an important parameter for the evaluation of the recognition ability of a separation technique; however, understanding the absolute purity of the optical isomers remains a challenge. Wang et al.[23] developed the following equation to estimate the relative optical purity of the separated SWCNT isomers

$$CD_{norm} = (CD_{raw}/L_{CD})/(A_{E22}/L_{abs}) \quad (1)$$

where CD_{raw} is the CD intensity at the E_{22} wavelength, A_{E22} is the background-corrected absorption intensity at the E_{22} transition, and L_{CD} and L_{abs} are the path lengths of the optical cell used in the measurement of CD and absorbance, respectively. We employed this equation to evaluate the relative optical purities of the various (*n, m*) isomer fractions. Here, the A_{E22} values were acquired from their original absorption spectra (Supporting Information, Figures S4−7). The highest relative optical purities for the isomer fractions are listed in Table 1. In previous works,[6,23,26,27] only the relative purities of the (6, 5) isomer (20−36 mdeg) were reported because of the separation of limited optical isomers. Although the highest relative purity of the (6, 5) isomer (9.8 mdeg) in the present work is a little lower, the relative abundance of the enriched isomer is clear. More importantly, our technique can be used to separate a wider range of nanotube structures (9 distinct (*n, m*) species). The relative purities of the (6, 4) and (9, 4) isomers even are higher than that of the (6, 5) isomers. Another attractive feature of our technique is that it is iteratively repeatable. As demonstrated in Figure 1c, the isomers of (6, 5) SWCNTS were sorted across five columns. To improve the separation yield, we repeated the separation of the Column 7 fraction. The results show that the optical isomers were further separated, as demonstrated in Figure S8 (Supporting Information). This result suggests that repeating

dx.doi.org/10.1021/nl5025613 | Nano Lett. 2014, 14, 6237−6243

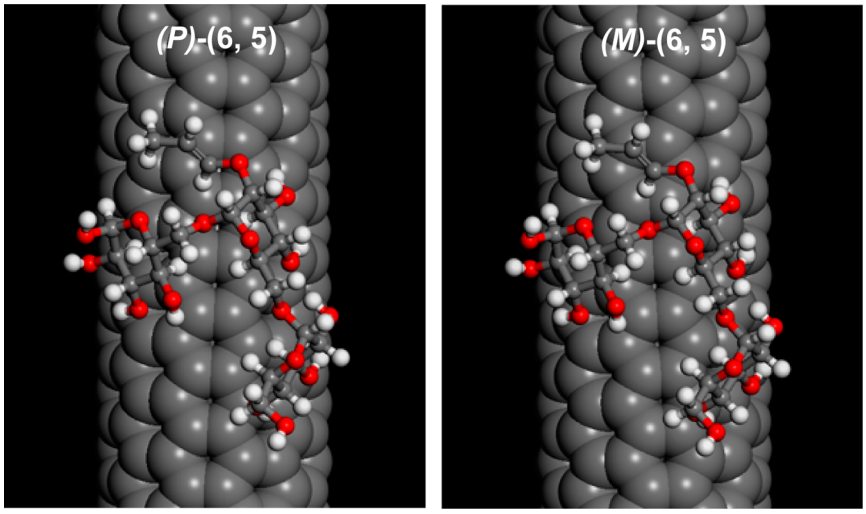


Figure 4. Schematic illustration of the interaction of the chiral left-handed (*M*) and right-handed (*P*) (6, 5)-SWCNTs with the chiral moieties (allyl dextran) of Sephacryl gel, which was generated by Materials Studio (Accelrys, San Diego, CA) software. The adsorption energy of allyl dextran on (*P*)-(6, 5) is 0.519 kcal/mol higher than that on the corresponding (*M*) structures. For the allyl dextran part, carbon atoms, oxygen atoms, and hydrogen atoms are represented as gray, red, and white spheres, respectively.

the sorting process to achieve improved yields and purity levels of optical isomers should be possible.

The isomer separation of single-chirality SWCNTs sufficiently indicates that the (*M*)- and (*P*)-isomers of SWCNTs have different interaction strengths with the gel. This interaction difference should be reflected in their optical purity. As demonstrated in Table 1 and in the upper panel in Figure 3a, the highest relative purities of the (*M*)- and (*P*)-isomers, even for the same chiral species separated by the two-step method, differ. The (*M*)-isomers for the (7, 5), (8, 4), and (9, 4) nanotubes exhibit a higher relative purity than their corresponding (*P*)-isomers. In contrast, the (*M*)-isomers for the (6, 5) and (7, 6) nanotubes exhibit a lower relative purity than their corresponding (*P*)-isomers. The higher-relative-optical-purity (*M*)/(*P*)-isomers agree well with their stronger interaction with the gel. We propose that a higher interaction strength of the (*M*)/(*P*)-isomers enhanced their adsorption into the gel columns and led to a higher optical purity than their corresponding (*P*)/(*M*) isomers. In contrast, a weaker interaction of the isomers with the gel resulted in a lower optical enrichment. Similar results were also observed in the (*n*, *m*) isomers separated using the temperature-control technique (Table 1 and the lower panel in Figure 3a); however, for more types of (*n*, *m*) nanotubes, only (*M*)- or (*P*)-isomers were obtained. In fact, the successful separation of the isomers of single-chirality SWCNTs also strongly depends on the difference in the interaction strengths of the isomers and other (*n*, *m*) nanotubes with the gel, which is determined by the smallest bond curvature of the nanotubes.[8,34] When the interaction difference is too small, separation of the isomers is difficult. In Figure 1a and c, we observe that the second (6, 4) fraction mixed with one of (6, 5) isomers, which explains why only either (*M*)- or (*P*)-enriched isomers for the (6, 4), (7, 3), (8, 6), and (8, 7) nanotubes were achieved using the two-step method. With the temperature-control technique, each type of isomer was separated from a much more complicated mixture. The interaction strength of the isomers with the gel would overlap with those of more different (*n*, *m*) nanotubes, leading to only either (*M*) or (*P*)-isomers being obtained for more distinct (*n*, *m*) SWCNTs.

To clarify the structure-dependent isomer recognition of gel column chromatography and thus the separation mechanism, we analyzed the relationship of the highest relative purity of each (*n*, *m*)-isomer with their physical structures. As observed in Figure 2c, nine distinct (*n*, *m*) species have a consistent magnitude order in their diameters and smallest C−C bond curvatures. We described the highest relative purity distribution of the separated isomers as a function of the smallest C−C bond curvatures and chiral angles (Figure 3b). Notably, both the bond curvatures and chiral angles strongly affect the purities of the separated isomers. For the nanotubes with chiral angles of 20−30° such as (6, 4), (6, 5), (7, 5), (7, 6), (8, 6), and (8, 7), the highest relative optical purities of the isomers separated by the two-step method first increase and then decrease with an increase in the smallest C−C bond curvature radius. In our previous work,[8] an increase in the smallest bond curvature radius caused a decrease the interaction strength of the nanotubes with the gel. This result indicates that an appropriate interaction strength is important for the enhancement of the isomer recognition of gel chromatography. As shown in Figure 3b, most of the isomers separated by the temperature-control technique exhibit higher optical purity than those sorted by the two-step method at room temperature, although the temperature-controlled separation is a single step. As demonstrated in our previous work,[34] temperatures can modify the SDS coverage or thickness on nanotube surfaces, leading to changes in their interaction with the gel. We therefore believe that the interaction control of (*n*, *m*) nanotubes with the gel can enlarge the differences in the interactions of the two isomers for a (*n*, *m*) SWCNT with the gel. On the basis of this result, we can expect that improved isomer purity and additional isomer separation could be achieved by controlling the interaction between nanotubes and the gel through variation of the temperature and SDS concentration.

As illustrated in Figure 3b, for nanotubes with similar smallest bond curvature radii such as the (6, 4), (7, 3) and (7, 5), (8, 4) nanotubes, the nanotubes with smaller chiral angles clearly exhibit a lower relative isomeric purity. This result implies that the chiral angles of (*n*, *m*) SWCNTs are another important factor for the isomer recognition of gel chromatog-

dx.doi.org/10.1021/nl5025613 | *Nano Lett.* 2014, 14, 6237−6243

raphy, which explains why the isomer separation of the (8, 3), (10, 2), (10, 3), and (12, 1) nanotubes with small chiral angles was not achieved even though these nanotubes have appropriate interaction strength with the gel and are able to be sorted from an SWCNT mixture. The previously discussed analysis sufficiently demonstrates that the diameters (smallest bond curvature radius) and chiral angles of (n, m) nanotubes are two critical factors for the isomer recognition of gel chromatography, which extraordinarily resembles the chiral molecular recognition of the isomers of SWCNTs.[6,16,21−27] In the present work, the chiral moieties of the gel should play a critical role in the recognition of the nanotube isomers.

As demonstrated in our previous work,[8,34] single-chirality separation by gel chromatography was achieved through the bond-curvature-dependent interaction of distinct (n, m) species with the gel. This interaction difference is derived from the variable coverage or thickness of the SDS coatings on the different (n, m) nanotube surfaces. The SDS coatings on the two isomers for the same (n, m) species should be the same because they have the same electronic properties and because SDS is an achiral molecule, that is, the isomer recognition ability of gel column chromatography does not originate from the different SDS coatings on the two isomers. The interaction difference of the optical isomers with the gel is reasonably concluded to result from the selective interaction of the chiral moieties with the isomers of (n, m) nanotubes. To demonstrate this hypothesis, we performed the simulation on the adsorption of the chiral moieties (allyl dextran part) of Sephacryl gel on the isomers of a SWCNT using Materials Studio (Accelrys, San Diego, CA) software. A schematic of allyl dextran stacking on the sidewalls of (6, 5)-isomers is shown in Figure 4. We can observe a similar conformation of allyl dextran on both the isomers. However, the adsorption energy of allyl dextran on (P)-(6, 5) is 0.519 kcal/mol higher than that on the corresponding (M) structures, confirming a big difference in the interactions of the two isomers with the chiral moieties of Sephacryl gel.[35,36] In contrast to (6, 5) nanotubes, the difference in the adsorption energy of allyl dextran on the isomers of (10, 2) nanotubes is only 0.073 kcal/mol, suggesting that their interaction difference with the chiral moieties of the gel is much smaller, which should be reason why the isomeric separation of (10, 2) nanotubes was not achieved.[35,36] It is not clear why the adsorption energy difference of allyl dextran on the optical isomers of a SWCNT varies with its geometric structures. We speculate that the adsorption energy depends on the nature of available adsorption sites on a SWCNT. A decrease in the adsorption energy difference of allyl dextran on (10, 2)-isomers should be the response to the distribution of available adsorption sites determined by their helical structures.

The role of the chiral moieties of Sephacryl gel in the isomeric separation gives deeper insights into the interactions among SWCNTs, surfactants, gel, and thus, the separation mechanism of SWCNT structures by gel chromatography. On the basis of this finding, we could further optimize the separation process of SWCNTs, paving the way for the single-structure separation of large-diameter SWCNTs. The selective interaction of SWCNT isomers with the chiral moieties of the gel suggests that they have promising applications in biosensors, biomedicine and separation of chiral drugs, and so forth.[37−39]

In summary, we have demonstrated that gel chromatography can be used for the high-efficiency separation of the optical isomers of single-chirality carbon nanotubes, truly achieving the single-structure separation of SWCNTs. Using this technique, we separated the optical isomers of nine distinct (n, m) single-chirality species, which is the maximum number of isolable species thus far. Moreover, gel chromatography has the advantages of low cost, technical simplicity, and industrial scale and, therefore, is superior to any reported method for the separation of optical isomers. This finding will accelerate the complete discovery of the physical properties of SWCNTs and their technical applications in the fields of optics, biosensors, materials science, nanotechnology, and so forth.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and Supplementary Figures S1−S8.This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: h-kataura@aist.go.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge Dr. J. Chen and M. Sun for their technical support for the simulation on the interaction of SWCNTs with allyl dextran. H.L. thanks support by the Recruitment Program of Global Youth Experts and the “100 talents project” of CAS. H.K. acknowledges support by JSPS KAKENHI Grant 25220602.

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