Structure Sorting of Large-Diameter Carbon Nanotubes by NaOH Tuning the Interactions between Nanotubes and Gel

Dehua Yang, Jinwen Hu, Huaping Liu, Shilong Li, Wei Su, Qian Li, Naigen Zhou, Yanchun Wang, Weiya Zhou, Sishen Xie, and Hiromichi Kataura*

The structure separation of synthetic single-wall carbon nanotube (SWCNT) mixture species with diameters larger than 1.2 nm still remains a challenge. Here, an NaOH-assisted gel chromatography method is used for the structure separation of the SWCNT mixture with a diameter range of 1.2–1.7 nm, in which NaOH is used to tune the interaction between distinct (*n, m*) SWCNTs and gel. Incrementally increasing NaOH concentration in SWCNT dispersion selectively enhances the adsorbability of different-structure SWCNTs and enlarges their interaction difference with gel, leading to their structure separation after applying into a gel column system. On this basis, a two-step method is developed for further improving the structure purity of the separated SWCNTs by combining overloading and stepwise elution. These results are well demonstrated by the optical spectra of the separated SWCNTs. This work paves a way for single-chirality separation of large-diameter SWCNTs using gel chromatography technique and is an advanced progress in the structure control of SWCNTs.

1. Introduction

As 1D structure, single-wall carbon nanotubes (SWCNTs) possess unique and superior optical and electrical properties, and have great potential applications in optoelectronic devices.[1–5] The electronic properties of an SWCNT are determined by its chiral angle and diameter. On the basis of its atomic arrangement structure, an SWCNT might be metallic or semiconducting. The band gaps of semiconducting SWCNTs are inversely proportional to their diameters. Previous results show that an SWCNT with larger diameter has a higher saturation current.[6–8] An increase in diameters would reduce the Schottky barrier between SWCNTs and metal electrodes,[6–8] which accelerates the source–drain tunneling of carriers and decreases on-state resistance. These results indicate that a larger diameter semiconducting SWCNT is more suitable for the fabrication of high-current and high-power devices. Some studies have suggested that the optimum diameter range of SWCNTs for transistor applications would lie from about 1.2 to 2 nm.[8] The advantages of higher carrier mobility and optical resonance in infrared region of larger diameter SWCNTs make them have a great potential application in infrared optical detectors.[9] However, the synthetic control of large-diameter SWCNTs with well-defined structures still remains a challenge. Recently, great efforts were made to develop various solution-based sorting methods of SWCNT structures, such as density gradient ultracentrifugation (DGU),[10,11] DNA-encapsulated separation,[12,13] and aqueous two-phase extraction (ATPE),[14,15] and yield predominantly single-chirality species with diameter less than 1.1 nm. Most Recently, the DGU and ATPE techniques were optimized and achieved the structure separation of the SWCNTs with diameters larger than 1.2 nm.[16,17] However, these two methods suffer from high cost, complicated separation process or low efficiency because multiple iterations have

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Dr. D. H. Yang, Dr. J. W. Hu, Prof. H. P. Liu, Dr. S. L. Li, Dr. W. Su,
Dr. Q. Li, Dr. Y. C. Wang, Prof. W. Y. Zhou, Prof. S. S. Xie
Beijing National Laboratory for Condensed Matter Physics
Institute of Physics
Chinese Academy of Sciences
Beijing 100190, China
E-mail: liuhuaping@iphy.ac.cn

Dr. D. H. Yang, J. W. Hu, Prof. H. P. Liu, Dr. S. L. Li, Dr. W. Su,
Dr. Q. Li, Dr. Y. C. Wang, Prof. W. Y. Zhou, Prof. S. S. Xie
Beijing Key Laboratory for Advanced Functional Materials
and Structure Research
Beijing 100190, China

Dr. D. H. Yang, Prof. H. P. Liu, Dr. S. L. Li, Dr. W. Su,
Prof. W. Y. Zhou, Prof. S. S. Xie
School of Physics Science
University of Chinese Academy of Sciences
Beijing 100049, China

Prof. H. P. Liu, Prof. S. S. Xie
Collaborative Innovation Center of Quantum Matter
Beijing 100190, China

J. W. Hu, Prof. N. G. Zhou
School of Materials Science and Engineering
Nanchang University
Nanchang 30031, China

Prof. H. Kataura
Nanomaterials Research Institute
National Institute of Advanced Industrial Science and Technology (AIST)
Tsukuba 305-8565, Japan

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201700278.

DOI: 10.1002/adfm.201700278

to be performed for the achievement of the structure separation of the SWCNTs, hindering the mass production of tight-distribution semiconducting SWCNTs for the technical applications. A simple, high-efficiency and low-cost structure sorting method is highly desirable for the separation of the SWCNTs with diameters larger than 1.2 nm.

In our previous work, the gel chromatography technique was demonstrated to be a simple, high-efficiency and low-cost for the separation of SWCNTs with diameters less than 1.1 nm,[18,19] in which sodium dodecyl sulfate (SDS) was used to tune the interaction between SWCNTs and gel. SDS is an anionic surfactant, which consists of 12-carbon tail attached to a sulfate group. In an aqueous solution of the SDS-dispersed SWCNTs, the hydrophobic alkyl group of SDS prefers to interact with SWCNT surfaces while the hydrophilic anionic "head group" with negative charges points toward water. Because of surface negative charge repulsion between nanotubes, they were dispersed into individuals in the solutions. The density of SDS on a nanotube is strongly dependent on its smallest C—C bond curvatures, which inversely determines its interaction with the SDS-functionalized gel medium. When the SDS-dispersed SWCNTs are loaded into a multistage gel column system, the distinct (*n, m*) species can be sorted across different columns because of their different interactions with gel. Recently, gel chromatography methods were further optimized to effectively amplify the interaction difference among various (*n, m*) SWCNT species with gel by overloading,[18] temperature,[19] ethanol,[20] pH,[21] and salts[22] and the separation yield of SWCNTs was improved greatly, even industrial separation of single-chirality SWCNTs and their optical isomers was achieved by introducing surfactant mixture.[23–26] However, the structure separation of the SWCNTs with diameters larger than 1.1 nm is not addressed yet. There are three possible reasons: (i) surfactant molecules prefer to adsorb on the larger-diameter SWCNTs, leading to their weaker interaction with gel; (ii) the population of SWCNTs with similar diameter increases as diameter increases; and (iii) the interaction difference among SWCNTs with the gel decreases as diameter increases.

In the present work, we report the separation of large-diameter SWCNTs (>1.2 nm) by the NaOH-assisted gel chromatography technique, in which NaOH is used to tune the interaction of SWCNTs with gel. Previous study revealed that large-diameter SWCNTs were more easily oxidized in acidic and even neutral solutions.[27,28] Such an oxidation of SWCNTs in acidic environment could reduce their adsorbility to gel.[21,22] On the basis of the results, we proposed that the interaction of large-diameter SWCNTs with gel could be tuned by NaOH neutralizing with H^+ ions in aqueous solution to prevent the oxidation of SWCNTs and amplify the interaction difference among various (*n, m*) SWCNTs with gel.[22] In this work, we systematically explored the effect of NaOH on the interaction between large-diameter SWCNTs (>1.2 nm) and gel and found that the introduction of NaOH could selectively enhance the interaction of SWCNTs with gel which was strongly dependent on the NaOH concentration. Based on this finding, we developed an NaOH-assisted gel chromatography technique and achieved the structure separation of large-diameter SWCNTs (>1.2 nm) by incrementally increasing the concentration of NaOH in SWCNT dispersion to finely tune their interactions with gel. The structure purity of the separated nanotubes has further been improved by a two-step method of combing overloading and stepwise elution. Compared with the DGU and ATPE techniques, the semiconducting purities of the separated nanotubes are comparable. The structure distributions of the separated SWCNTs are very tight, highly enriched in only three or four distinct species. More importantly, the yield of separating SWCNTs by our present strategy can reach mg-scale per day, which is much higher than the other two methods. Our present work is an advanced progress in the structure separation of SWCNTs, accelerating their application in devices.

2. Results and Discussion

2.1. The Effect of NaOH on the Interaction of SWCNTs with Gel

The arc-discharge produced SWCNTs (Diameter 1.2–1.7 nm, Pure SWCNTs, AP23-146, NanoIntegris) with a diameter range of 1.2–1.7 nm were used as the starting materials. The SWCNT dispersion with 1 wt% SDS was prepared by ultrasonication, centrifugation, and gel filtration processes (see details in the Experimental Section). The as-prepared SWCNT dispersion of 32 mL with 1 wt% SDS was divided into 8 mL aliquots and diluted into 0.6 wt% SDS. NaOH with various concentrations from 0 to 0.5×10^{-3} M was introduced into these SWCNT fractions to investigate its effect on the adsorbability of SWCNTs onto gel. Before separation, four same gel columns filled with allyl dextran-based gel beads (Sephacryl S-200, GE Healthcare) of 25 mL were prepared for parallel experiments. The adsorbed nanotubes were eluted and collected with a 5 mL aqueous solution of 5 wt% SDS. The optical absorption spectra are presented in **Figure 1**a. The peaks at the wavelengths from 900 to 1050 nm and from 350 to 650 nm represent the second (S_{22}) and third optical (S_{33}) transition of the semiconducting SWCNTs with diameters ranging from 1.2 to 1.7 nm, while the absorption peaks in the range of 600–800 nm denote the first optical transition (M_{11}) of metallic nanotubes. With an increase in the concentration of NaOH from 0 to 0.5×10^{-3} M, the absorbance of the S_{22} and S_{33} peaks gradually increase, accompanying with a redshift of S_{22} peaks and an increase in absorbance peaks in S_{33} region. Generally speaking, the S_{22} absorption peaks of larger diameter SWCNTs correspond to longer optical absorption wavelengths. The results indicate that increasing NaOH concentration could induce the enhancement of the interactions of SWCNTs and gel, leading to an increase in the quantity and types of the adsorbed nanotubes.[18,19]

We also explored the NaOH effect on the adsorbability of SWCNTs into gel under various SDS concentations of 0.4, 0.8, and 1 wt% using the same procedure. Figure S1 in the Supporting Information shows the optical absorption spectra of the adsorbed semiconducting SWCNTs under different NaOH concentrations at each SDS concentration. Compared with the case of 0.6 wt% SDS, the similar effect of NaOH on the adsorbability of SWCNTs onto gel is observed. Increasing NaOH concentration induced the adsorption of more types and quantity of SWCNTs into gel columns (Figure 1b,c). However, for high-concentration SDS such as 0.8 and 1 wt%, the quantity of the adsorbed nanotubes is very small, and under

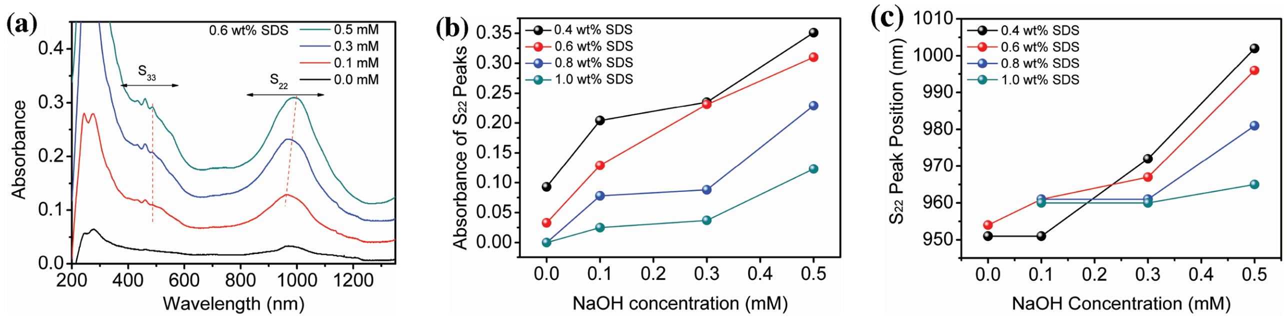

Figure 1. Effect of NaOH on the adsorbability of SWCNTs into gel. a) Optical absorption spectra of the adsorbed SWCNTs under various NaOH concentrations. b) The S_{22} peak absorbance of the adsorbed SWCNTs functions as the NaOH concentrations. c) The centered position of S_{22} peak functions as the NaOH concentrations.

the NaOH concentrations lower than 0.1×10^{-3} M, no nanotubes can adsorb into gel columns, as shown in Figure 1b. The NaOH cocentration has a weaker effect on the adsorbability of SWCNTs (Figure 1b,c). With a decrease in SDS concentration, the optcial absorbance and S_{22} peak shift of the adsorbed nanotubes changed more greatly with an increase in the NaOH concentration, as shown in Figure 1b,c. In other words, NaOH have a great effect on the adsorbability of SWCNTs under the SDS concentrations of 0.4 and 0.6 wt% because a low-SDS density on the nanotube surfaces can be more efficiently tuned and thus their interaction with the gel. Nevertheless, in the case of 0.4 wt% SDS, the absorption peak of metallic SWCNTs can be clealy observed even without NaOH (Figure S1a, Supporting Information).

On the basis of the effect of NaOH on the adsorbability of SWCNTs onto gel, we propose that a stepwise increment in the concentration of NaOH in SWCNT dispersion could selectively enhance the interaction between larger diameter SWCNTs and gel, leading to their structure separation. However, considering the adsorption of the metallic SWCNTs onto gel in the case of 0.4 wt% SDS and weak adsorbability of semiconducting SWCNTs under the SDS concnetrations of 0.8 and 1.0 wt%, 0.6 wt% is the optimal SDS concentration for the structure separation of the SWCNTs with a diameter range from 1.2 to 1.7 nm.

2.2. Diameter Separation by NaOH Finely Tuning the Interaction between Nanotubes and Gel

In order to separate SWCNT structures, we designed an experiment in which the NaOH concentration in the SWCNT dispersion with 0.6 wt% SDS was incrementally increased from 0 to 0.5×10^{-3} M with a step of 0.05×10^{-3} or 0.1×10^{-3} M. At each NaOH concentration, 32 mL SWCNT dispersion was applied into multistage gel columns until no nanotubes could be adsorbed. Subsequently, the NaOH concentration in the flow-through fraction was increased to a higher concentration for the next separation using the same procedure. The gel columns were the same, each of which was prepared by filling a 50 mL syringe with 25 mL gel beads. The adsorbed nanotubes were eluted with an aqueous of 5 wt% SDS and fractionally collected with 5 mL solution.

The optical adsorption spectra for the adsorbed nanotubes at each concentration of NaOH are shown in **Figure 2** and Figure S2 in the Supporting Information. The S_{22} absorption peaks of the separated nanotubes are clearly different at various NaOH concentrations, indicating that the diameter separation of SWCNTs was achieved. Actually, the S_{22} peak shift at the same NaOH concentration is also observed. The lack of metallic peaks suggests that few metallic SWCNTs are present in the separated SWCNTs, indicating the separation of metallic and semiconducting SWCNTs was simultaneously achieved. The semiconducting SWCNT species were adsorbed in the index from relatively small to large diameter which is consistent with the results of the separation of small-diameter SWCNTs (0.75–1.1 nm) where smaller diameter semiconducting SWCNTs correspond to larger affinity to gel.[18,19,23] Raman spectra were also measured for the characterization of the separated nanotubes, as shown in Figure 2b. Compared with the initial SWCNT mixture, the peaks in the radial breathing mode (RBM) region of the separated nanotubes become sharp and narrow and shift from ≈185 to 155 cm^{-1} for the various SWCNTs fractions, corresponding to an increase in diameter.[29]

The clear S_{22} peak shift of the sorted SWCNT fractions under the same NaOH concentration (Figure 2 and Figure S2, Supporting Information) implies that the loading amount of the unsorted nanotubes is excessive (that is, overloading), which promotes the structure separation of SWCNTs. When the initially loading amount of SWCNTs was decreased, the S_{22} absorption peak shift for the sorted SWCNTs across different gel columns is less obvious under the same NaOH concentration (as shown in Figure S3, Supporting Information). These results further demonstrate that the introduction of NaOH enlarges the interaction difference among distinct SWCNTs with gel and the structure sorting of the large-diameter nanotubes could be achieved by simple overloading effect due to the competitive adsorption of different structure SWCNTs onto gel. The structure separation of SWCNTs was also achieved by incrementally increasing NaOH concentration in the 0.4 wt% SDS dispersed SWCNT solution. (Figure S4, Supporting Information).

2.3. Diameter Separation by Two-Step Separation

Although the structure separation of large-diameter SWCNTs has been achieved by a stepwise increase in the NaOH concentration, the separation process is still complicated because of a continuously tuning NaOH concentration in the flow-through

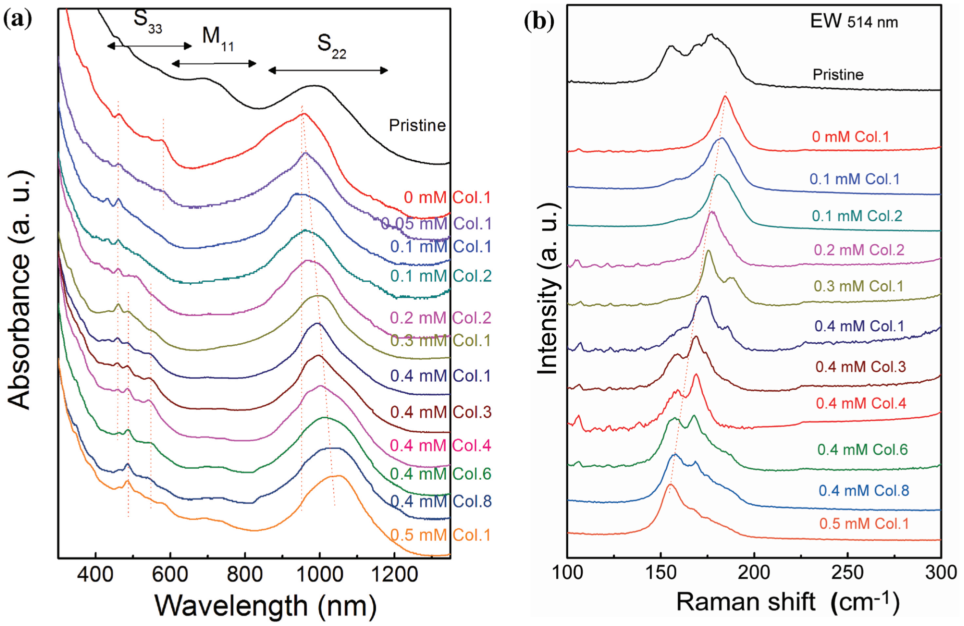

Figure 2. Optical characterizations of the separated SWCNTs by incrementally increasing NaOH concentration. a) Optical absorption spectra. b) Raman spectra with an excitation wavelength of 514 nm.

SWCNT fractions. Since the addition of NaOH effectively increases the interactions between large-diameter SWCNT species and gel beads, we can simplify the structure separation process by a stepwise elution with various SDS concentrations. Specifically, introducing NaOH into the nanotube dispersion enhanced the interaction between nanotubes and gel, and then the adsorbed nanotubes were eluted by a stepwise increase in the SDS concentration. This process is compatible with automatic chromatography system. The chirality purity of the separated nanotubes strongly depends on the structure distribution of the adsorbed nanotubes. A wider structure distribution of the adsorbed nanotubes would lead to a decrease in the structure purity of the separated nanotubes due to the mutual disturbance among the different structure SWCNTs. Accordingly, in order to improve the structure purity of the separated nanotubes, a preseparation of pristine nanotube mixture is necessary. As mentioned above, overloading can simply sort different-structure SWCNTs across the different gel columns by NaOH enhancing the interaction of SWCNTs with gel. We can expect to further improve the structure purity of the separated SWCNTs by a two-step method of combining overloading and stepwise elution.

In the first separation, we used the overloading method. 0.2×10^{-3} M NaOH was introduced into the SWCNT/0.6 wt% SDS dispersion for enhancing the interaction between SWCNTs and gel. After that, 32 mL SWCNT dispersion was applied into multistage gel columns, each of which was prepared by filling a 50 mL syringe with 25 mL Sephacryl gel. The adsorbed SWCNTs on each column were eluted by 2.5 wt% SDS solution. After flowing through several columns, the NaOH concentration was increased to a higher degree with a step of 0.2×10^{-3} M to induce the adsorption of more SWCNTs. Such parallel experiment was performed four times. The eluted SWCNTs from the same gel column were gathered and diluted to 0.6 wt% SDS for the second separation. **Figure 3** shows the optical characterization of the separated nanotubes in the first separation. The color of the eluted SWCNT solutions from different columns is distinct (as shown in Figure 3a,b), indicating their different structure distribution. The clear S_{22} peak redshift and S_{33} peak change in the absorption spectra (Figure 3c) evidence that the structure separation of SWCNTs was achieved. Additionally, the corresponding RBM peaks in the Raman spectra excited with a wavelength of 514 nm (Figure 3d) also exhibit a peak shift from 180 to 150 cm^{-1}, which further confirm the structure separation of SWCNTs. Note the yield of the separated SWCNTs can reach mg-scale per day by the present strategy (Figure 3b), because of simple and high-efficiency separation process. The separated SWCNTs with narrower structure distribution provide good starting materials for the second separation.

The second separation was performed by an automatic chromatography system (AVANT 150, GE Healthcare), in which the SDS concentration in the stepwise elution can be precisely tuned to desorb SWCNTs. A 25 cm long gel column was employed for the separation process which was prepared by filling an XK16/40 column (GE Healthcare) with 50 mL gel beads. We expect that the nanotubes with small interaction difference with gel can be separated by flowing through a long column. The separated SWCNT fractions in the first separation were concentrated and dispersed for the second separation. The SDS and NaOH concentrations were fixed at 0.6 wt% and 0.2×10^{-3} M in the SWCNT dispersion. The adsorbed SWCNTs were eluted and collected with 5 mL fractions by incrementally increasing SDS concentration in elution solutions.

The optical absorption spectra of the sorted SWCNT fractions in the second separation (**Figure 4**) exhibit sharper and narrower S_{22} peaks, indicating that a further separation of SWCNT structures was achieved. Comparison between Raman spectra before and after the second separation also confirms that the structure

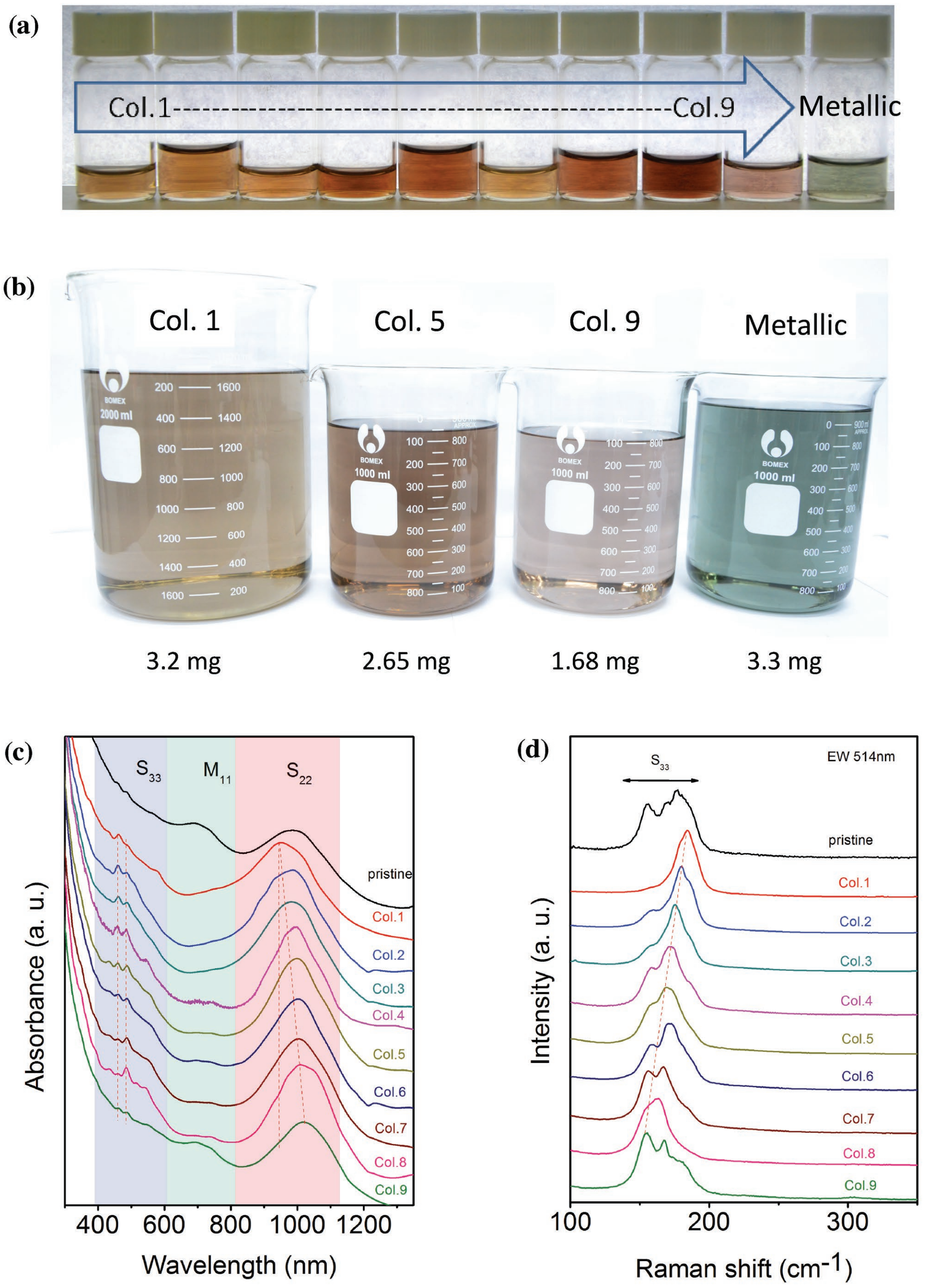

Figure 3. Optical characterization of the separated nanotube fractions across different gel columns by overloading method. a) Photograph of the separated semiconducting fractions from Col. 1 to Col. 9 (marked by blue arrow) and the unadsorbed metal fraction (the green fraction on the far right side). b) Solution photos of the large volumes of the separated nanotubes, which were separated within 3 d. The mass of the SWCNTs in each beaker was evaluated by their optical spectra.[30] The yield can reach mg-scale per day. c) Optical absorption spectra. The peak shift is marked by a dash line. d) Raman spectra at an excitation wavelength of 514 nm. The black line at the top shows the Raman spectrum of the pristine materials.

distribution after the second separation becomes much narrower (Figure S5, Supporting Information). The semiconducting purities of the separated SWCNTs were evaluated by the area ratio of the S_{22} and M_{11} peaks. The highest purity can be in excess of 99% (Figure S6, Supporting Information) because of the lack of the metallic peaks. Interestingly, the SWCNTs eluted by lower concentration SDS solution exhibit shorter wavelength absorption peaks in the S_{22} region, while those eluted by higher concentration SDS solution exhibit a longer wavelength S_{22} peaks. The results are contrary to the previous results, in which SDS molecules selectively prefer to adsorb onto the larger diameter nanotubes.[8,9] The reasons are unclear yet. One of the possible reasons is that the later eluted nanotubes are present in the form of small bundles, which have stronger interaction

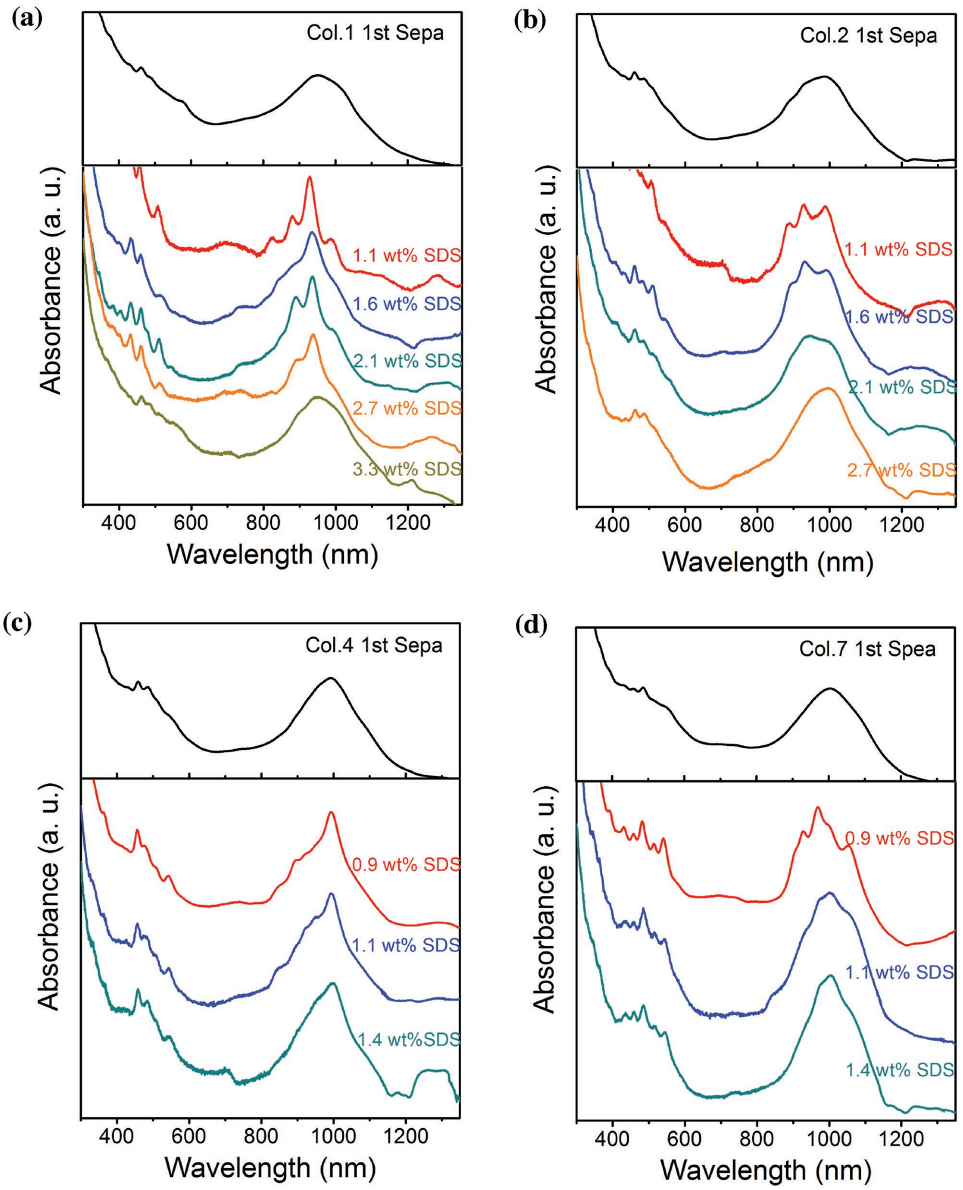

Figure 4. Optical adsorption spectra of the fractions eluted by various concentration of SDS from Col. 1, Col. 2, Col. 4, and Col. 7 in second separation. The spectra were normalized at S_{22} peaks (800–1300) and offset for comparison.

with gel (see Figure S7, Supporting Information). The optical spectra of the sorted fractions across different columns are integrated in **Figure 5**a and Figure S8a in the Supporting Information and exhibit sharp and narrow S_{22} peaks shifting from 890 to 1050 nm and covering the whole S_{22} peak range of the raw SWCNTs. The corresponding Raman spectra in the RBM region are shown in Figure 5b and Figure S8b in the Supporting Information. The sharper and distinct RBM peaks are another solid evidence for the structure separation. In Figure S8 in the Supporting Information, although some fractions exhibit similar optical absorption spectra due to spectral congestion, their corresponding Raman spectra are obviously different, this helpfully distinguishes their diameter distribution.[31] In order to evaluate the chirality distribution of the separated nanotubes, we analyzed the S_{22} peaks in the absorption spectra of the separated SWCNTs using the PeakFit software.[18] The purity of each (n, m) fraction was computed as the ratio of the area of the (n, m) species to the sum of the peak areas (Purity $(n1, m1)$ = Area $(n1, m1)/\Sigma$Area (n, m)).[18] The chiral index for each S_{22} peak was assigned on the basis of the optical transition energies of the second sub-band gap for each (n, m).[31] The peaks indicated with stars were difficulty assigned a pair of chiral index because they correspond to the optical transition energies of multiple (n, m) species. As shown in Figure 5c–f, the chirality distributions of the separated nanotubes were very narrow.[31] For example, the eluted nanotubes from column 1 with 1.1 wt% SDS were enriched in (12, 7), (13, 6), and (15, 4) (Figure 5c). They accounted for about 74.4%, among which the (12, 7) nanotubes reached about 39.7%. And those eluted from column 1 with 2.1 wt% SDS mainly contained (12, 7), (17, 1), and (15, 4)

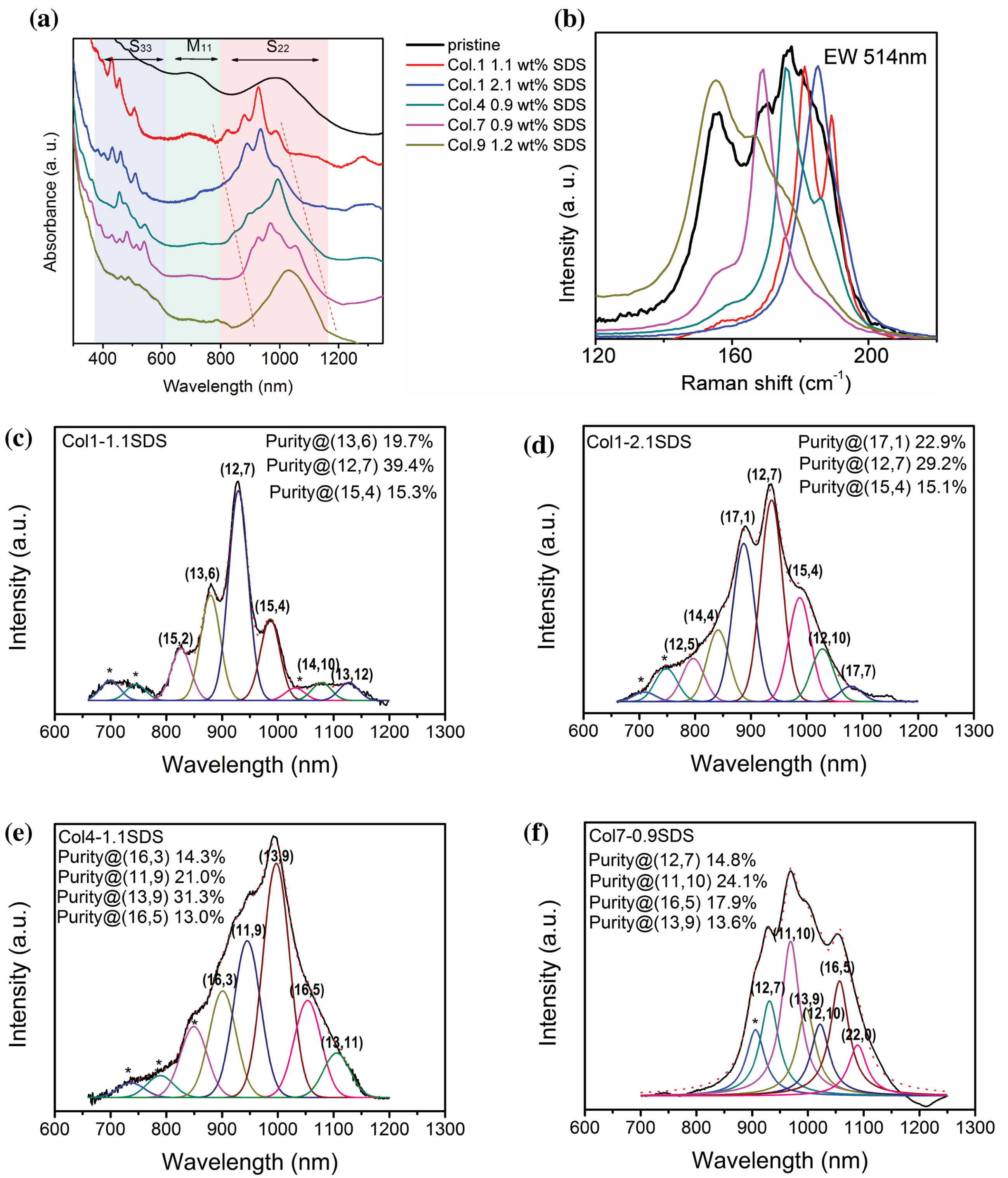

Figure 5. Optical characterizations of the separated semiconducting SWCNTs by a two-step method of combing overloading and stepwise elution. a) Optical adsorption spectra. The spectra were normalized at S_{22} peaks (800–1300) and offset for comparison. b) Normalized Raman spectra for the corresponding fractions in (a). c–f) Evaluation of the purities of the separated (*n*, *m*) nanotubes. The PeakFit software was used to simulate the S_{22} peaks in the absorption spectra of the sorted (*n*, *m*) nanotubes. The purity of each (*n*, *m*) fraction was computed as the ratio of the area of the (*n*, *m*) species to the sum of the peak areas (Purity (*n*1, *m*1) = Area (*n*1, *m*1)/ΣArea (*n*, *m*)).[18] The chiral index for each S_{22} peak was assigned on the basis of the optical transition energies of the second sub-band gap for each (*n*, *m*).[30] The peaks indicated with stars were difficultly assigned a pair of chiral index because they corresponds to the optical transition energies of multiple (*n*, *m*) species.

species, which accounted for about 67.2% (Figure 5d). The fraction eluted from column 4 with 1.1 wt% SDS had about 79.4% of the (16, 3), (11, 9), (13, 9), and (16, 5) species (Figure 5e). The components of the nanotube fraction eluted from column 7 with 0.9% SDS are about 70.4% of the (11, 10), (12, 7), (16, 5), and (13, 9) species (Figure 5f). The results quantitatively presented that the separated nanotubes mainly contained three or four types of (*n, m*) species.

As described the above results, it is obvious that the introduction of NaOH significantly enhanced the adsorbability of large-diameter SWCNTs on gel beads and enlarges the difference in their interaction with gel. Previous work reports that the presence of H^+ and O_2 could induce the oxidation (or protonation) of SWCNTs and produce hydroperoxide carbocations.[21,22] The reaction proceeds as follow:[28] SWCNTs (reduced) + O_2 + H^+ → $SWCNTs^+$ (oxidized) + H_2O. The positive charges on the surface of nanotubes would screen the negative charges of the SDS head groups, leading to the larger coverage or higher density SDS on the nanotube surfaces and thus a decrease in their interaction with gel.[21,22] The oxidation or protonation of SWCNTs is substantially determined by their reduction potentials which decrease with their band gaps. Larger diameter semiconducting SWCNTs are more easily oxidized due to their smaller band gaps and thus larger SDS coverage and weaker adsorbability onto gel.[21] The introduction of OH^- could neutralize H^+ ions in SWCNT dispersion and deprotonates or reduces SWCNTs.[22,27] Contrary to the oxidation process, the reduction process prefers to occur on the smaller diameter SWCNTs with larger band gaps. A stepwise addition of NaOH into an SWCNT dispersion would first induce the reduction of the smaller diameter SWCNTs and subsequently the larger diameter SWCNTs. Our experimental results show that a stepwise increase in the NaOH concentration led to the successive adsorption of semiconducting SWCNTs in the order from smaller to larger diameter (Figures 1 and 2), which is well consistent with the separation model we proposed.

The oxidation and reduction of the SWCNTs can be directly observed by bleaching or recovering of their optical absorbance.[27,28] In order to confirm that the reduction of the SWCNTs occurs by the addition of NaOH in our present work, we explored the effect of NaOH on the optical absorbance of the SWCNTs. Before adding NaOH, the SWCNT dispersion with 1 wt% SDS was prepared by ultrasonication, centrifugation, and gel filtration processes. As shown in Figure S9 in the Supporting Information, with an increase in the NaOH concentration, the optical absorbance in the S_{22} region of the SWCNTs increases clearly. Interestingly, the defects of the SWCNTs were also reduced during ultrasonication process at the presence of NaOH. As shown in Figure S10 in the Supporting Information, the normalized Raman spectra display that the D peak intensity of the as-dispersed SWCNTs decreases when NaOH was present during ultrasonication process. We believe that the suppression of the physical defects should result from the oxidation prevention of the SWCNTs by NaOH. These results further indicate that the reduction of the SWCNTs by NaOH should play dominant roles in tuning the interaction between SWCNTs and gel in our present work.

Temperature is an important factor affecting the oxidation of SWCNTs and thus determines the coverage of SDS on SWCNTs and their adsorbability onto gel. It was reported that the reduction potential of O_2 and H^+/H_2O varied with temperature.[32] The oxidation of SWCNTs in SDS solution can thus be controlled by temperature, which inversely could tune the interactions between large-diameter SWCNTs and gel beads. Our previous work has demonstrated that temperature affected the oxidation of different SWCNTs and thus the selective adsorption of SDS around SWCNTs and enlarged their interaction difference with gel.[19] Although we kept the temperature unchanged through the whole experiment, we can expect that temperature could be utilized to further improve the structure purity of the separated large-diameter SWCNTs in the future study.

3. Conclusion

In summary, we demonstrated the ability of NaOH tuning the interaction of SWCNTs with gel and achieved the structure separation of large-diameter SWCNTs ranging from 1.2 to 1.7 nm by using gel chromatography technique. The introduction of NaOH could reduce the oxidation of SWCNTs, increase the interaction of large-diameter SWCNTs with gel and lead to selective adsorption of different-structure SWCNTs and achieve their structure separation. We believe that by tuning the concentration of OH^- more precisely, the structure purity of the separated SWCNTs can be further improved. The present strategy has the advantages of low cost, technical simplicity, and high throughputs and provides a brand-new approach for the structure separation of large-diameter SWCNTs. Our present work will accelerate the property study of SWCNTs and advance their technical applications in the fields of carbon-based electronics, optoelectronics, bioimaging, and so forth.

4. Experimental Section

Dispersion and Purification of SWCNTs: SWCNTs produced via arc-discharge (Diameter 1.2–1.7 nm, Pure SWCNTs, AP23-146, NanoIntegris) were used as starting materials. 6 mg of AP-SWCNTs were sheared and dispersed in H_2O (20 mL) with 1 wt% SDS (99%, Sigma-Aldrich) using a tip homogenizer (Sonifire 450D, Branson) at 30% power for 2.5 h. During sonication, SWCNT solution was immersed in a water bath at 15 °C. After sonication, the dispersion was centrifuged at 210 000 g for 30 min in the ultracentrifuge (S50A, Hitachi CS150FNX). The upper 80% of supernatant was recovered for further purification by gel filtration. The gel column for the nanotube purification was prepared by filling 30 mL of gel beads (Sephacryl S-200 HR, GE Healthcare) into a 50 mL medical syringe. The centrifuged nanotube supernatant was applied into the column to remove amorphous carbon and collected as 32 mL. Without the gel column purification, the dispersed SWCNTs cannot adsorb into gel columns (as shown in Figures S11 and S12, Supporting Information). Before the loading of the nanotubes, the gel column was equilibrated by SDS solution (1 wt%).

The Effect of NaOH on Structure Separation: The purified SWCNT dispersion was separated into four aliquots and their SDS concentrations were separately tuned into 0.4, 0.6, 0.8, and 1 wt% SDS by adding pure H_2O. In order to investigate the effect of NaOH on the adsorbability of nanotubes into gel columns, each of the nanotube solutions with various SDS concentrations was divided into four aliquots and the NaOH concentration were tuned into 0, 0.1×10^{-3}, 0.3×10^{-3}, and 0.5×10^{-3} M. Next, each fraction of the nanotube dispersion was applied into the same gel columns. The adsorbed nanotubes were eluted by an aqueous solution of SDS (5 wt%). To compare the amount of adsorbed nanotubes by optical absorbance, the eluted nanotubes were collected with a volume of 5 mL. The effect of NaOH on the adsorbability of SWCNTs is shown in Figure 1.

Structure Separation of SWCNTs by NaOH Tuning the Interaction: The separation of carbon nanotubes was performed by a stepwise increase in NaOH concentration. The raw material was dispersed, centrifuged, and purified by gel filtration as described above. The 32 mL dispersion was diluted to 0.6 wt% SDS using pure water and applied to a 50 mL syringe filled with 30 mL gel beads after equilibrium. Then, 0.6 wt% SDS solution was injected into the column to elute the unadsorbed SWCNTs. The adsorbed SWCNTs were eluted by 5 wt% SDS solution, while the unadsorbed SWCNTs were collected and applied to the next column as starting material until no SWCNTs could adsorb into gel column. Subsequently, NaOH was added to the unadsorbed SWCNT dispersion with a step of 0.05×10^{-3} or 0.1×10^{-3} M. The NaOH in equilibration solution was kept consistent with the corresponding SWCNT dispersion. At each NaOH concentration, the SWCNT dispersion was repeatedly loaded into the gel columns until no nanotubes can be adsorbed.

Two-Step Separation of SWCNTs by the Addition of NaOH: 16 mL parent dispersion with 1 wt% SDS was further purified by flowing through a gel column and collected as 32 mL and diluted to 0.6 wt% SDS. For the structure separation of SWCNTs, the NaOH concentration was tuned to 0.2×10^{-3} M to increase their interaction with gel. The nanotube dispersion with NaOH was applied to multistage gel columns for the first separation of nanotubes. Each column was filled with 30 mL gel beads. When the amount of adsorbed SWCNTs decreases dramatically, the concentration of NaOH increased with a step of 0.2×10^{-3} M. The final NaOH concentration reached 0.6×10^{-3} M. The adsorbed nanotubes were eluted with solution of SDS (2.5 wt%) without NaOH. Four parallel experiments were performed. The separated SWCNT fractions from the same gel columns were gathered for the second separation.

In the second separation, each separated SWCNT fraction in the first separation was diluted to 0.6 wt% SDS and concentrated using ultracentrifugation. The concentrated nanotubes were further dispersed by ultrasonication. The NaOH concentration was tuned to 0.2×10^{-3} M. A gel column was prepared by filling 50 mL gel beads into an XK16/40 (40 cm in length, GE Healthcare) and then connected to an automated chromatography system (AVANT 150, GE Healthcare). The as-prepared nanotube dispersion was loaded into the gel column and the adsorbed SWCNTs were eluted with the aqueous solution of SDS with 0.2×10^{-3} M NaOH by a stepwise increase in SDS concentration. The whole experiment was performed in a homemade thermostat to exclude the effects of temperature fluctuation.

Characterization: Optical absorbance spectra were measured using an ultraviolet–near-infrared spectrophotometer (UV-3600, Shimadzu). Raman spectra for 514 nm excitation were measured using a confocal Raman microscope (HR800, Horiba) equipped with a charge-coupled device detector.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

D.H.Y. and J.W.H. contributed equally to this work. This work was supported by the National Natural Science Foundation of China (Grant Nos. 51472264, 11634014, and 51361022) and the Key Research Program of Frontier Sciences, CAS, Grant No. QYZDB-SSW-SYS028. H.L. thanks support by the Recruitment Program of Global Youth Experts and the "100 talents project" of CAS.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon nanotubes, gel chromatography NaOH, structure separation

Received: January 17, 2017
Revised: July 17, 2017

[1] E. T. Thostenson, Z. F. Ren, T. W. Chou, *Compos. Sci. Technol.* **2001**, *61*, 1899.
[2] M. Engel, J. P. Small, M. Steiner, M. Freitag, A. A. Green, M. C. Hersam, P. Avouris, *ACS Nano* **2008**, *2*, 2445.
[3] P. W. Barone, S. Baik, D. A. Heller, M. S. Strano, *Nat. Mater.* **2005**, *4*, 86.
[4] R. M. Jain, R. Howden, K. Tvrdy, S. Shimizu, A. J. Hilmer, T. P. McNicholas, K. K. Gleason, M. S. Strano, *Adv. Mater.* **2012**, *24*, 4436.
[5] A. Javey, J. Guo, Q. Wang, M. Lundstorm, H. Dai, *Nature* **2003**, *424*, 654.
[6] M. Ganzhorn, A. Vijayaraghavan, S. Dehm, F. Hennrich, A. A. Green, M. Fichtnert, A. Voigt, M. Rapp, H. von Lohneysen, M. C. Hersam, M. M. Kappes, R. Krupket, *ACS Nano* **2011**, *5*, 1670.
[7] Z. Chen, J. Appenzeller, J. Knoch, Y. Lin, P. Avours, *Nano Lett.* **2005**, *5*, 1497.
[8] G. S. Tulevski, A. D. Franklin, D. Frank, J. M. Lobez, Q. Cao, H. Park, A. Afzail, S. Han, J. B. Hannon, W. Haensch, *ACS Nano* **2014**, *8*, 8730.
[9] X. Zhou, J. Y. Park, S. Huang, J. Liu, P. L. McEuen, *Phys. Rev. Lett.* **2005**, *95*, 146805.
[10] A. A. Green, M. C. Hersam, *Adv. Mater.* **2011**, *23*, 2185.
[11] S. Ghosh, S. M. Bachilo, R. B. Weisman, *Nat. Nanotechnol.* **2010**, *5*, 443.
[12] M. Zheng, A. Jagota, M. S. Strano, A. P. Santos, P. Barone, G. Chou, B. A. Diner, M. S. Dresselhaus, R. S. Mclean, G. B. Onoa, G. G. Samsonidze, E. D. Semke, M. Usrey, D. J. Walls, *Science* **2003**, *302*, 1545.
[13] M. Zheng, A. Jagota, E. D. Semke, B. A. Diner, R. S. McLean, S. R. Lustig, R. E. Richardson, N. G. Tassi, *Nat. Mater.* **2003**, *2*, 338.
[14] J. A. Fagan, C. Y. Khripin, C. A. Silvera Batista, J. R. Simpson, E. H. Haroz, A. R. Hight Walker, M. Zheng, *Adv. Mater.* **2014**, *26*, 2800.
[15] H. Gui, J. K. Streit, J. A. Fagan, A. R. Hight Walker, C. Zhou, M. Zheng, *Nano Lett.* **2015**, *15*, 1642.
[16] J. A. Fagan, E. H. Haroz, R. Ihly, H. Gui, J. L. Blackburn, J. R. Sompson, S. Lam, A. R. Hight Walker, S. K. Doorn, M. Zheng, *ACS Nano* **2015**, *9*, 5377.
[17] J.-W. T. Seo, N. L. Yoder, T. A. Shastry, J. J. Humes, J. E. Johns, A. A. Green, M. C. Hersam, *J. Phys. Chem. Lett.* **2013**, *4*, 2805.
[18] H. Liu, D. Nishide, T. Tanaka, H. Kataura, *Nat. Commun.* **2011**, *2*, 309.
[19] H. Liu, T. Tanaka, Y. Urabe, H. Kataura, *Nano Lett.* **2013**, *13*, 1996.
[20] X. Zeng, J. Hu, X. Zhang, N. Zhou, W. Zhou, H. Liu, S. Xie, *Nanoscale* **2015**, *7*, 1627.
[21] B. S. Flavel, K. E. Moore, M. Pfohl, M. M. Kappes, F. Hennrich, *ACS Nano* **2014**, *8*, 1817.

[22] A. Hirano, T. Tanaka, Y. Urabe, H. Kataura, *ACS Nano* **2013**, *7*, 10285.
[23] H. Liu, T. Tanaka, H. Kataura, *Nano Lett.* **2014**, *14*, 6237.
[24] C. A. Silvera-Batista, D. C. Scott, S. M. McLeod, K. J. Ziegler, *J. Phys. Chem. C* **2011**, *115*, 9361.
[25] Y. Yomogida, T. Tanaka, M. Zhang, M. Yudasaka, X. Wei, H. Kataura, *Nat. Commun.* **2016**, *7*, 12056
[26] X. Wei, T. Tanaka, Y. Yomogida, N. Satio, R. Saito, H. Kataura, *Nat. Commun.* **2016**, *7*, 12899.
[27] G. Dukovic, B. E. White, Z. Zhou, F. Wang, S. Jockusch, M. L. Steigerwaid, T. F. Heinz, R. A. Friesner, N. J. Turro, L. E. Brus, *J. Am. Chem. Soc.* **2004**, *126*, 15269.
[28] M. Zheng, B. A. Diner, *J. Am. Chem. Soc.* **2004**, *126*, 15490.
[29] M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, *Phys. Rep.* **2005**, *409*, 47.
[30] S. Attal, R. Thiruvengadathan, O. Regev, *Anal. Chem.* **2006**, *78*, 8098.
[31] R. B. Weisman, S. M. Bachilo, *Nano Lett.* **2003**, *3*, 1235.
[32] A. Nish, R. J. Nicholas, *Phys. Chem. Chem. Phys.* **2006**, *8*, 3547.