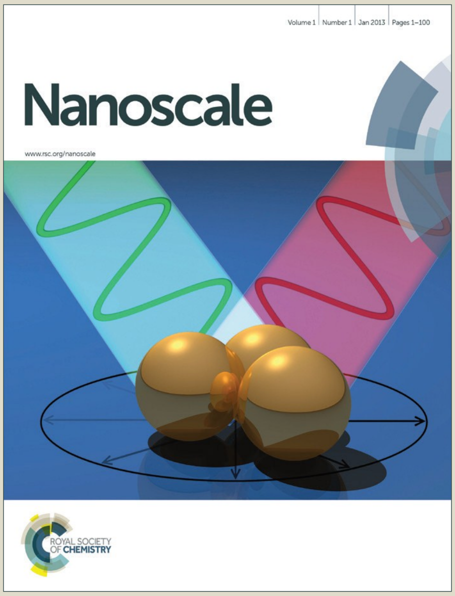
Nanoscale

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/nanoscale

Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ethanol-assisted gel chromatography for single-chirality separation of carbon nanotubes†

Xiang Zeng,[a,b] Jinwen Hu,[a,b] Xiao Zhang,[b,c] Naigen Zhou,*[a] Weiya Zhou,[b,c] Huaping Liu*[b,c,d] and Sishen Xie[b,c,d]

Surfactants or polymers are usually used for the liquid processing of carbon nanotubes for their structure separation. However, they are difficult to remove after separation, affecting the intrinsic properties and applications of the separated species. Here，we report an ethanol-assisted gel chromatography for the chirality separation of single-wall carbon nanotubes (SWCNTs), in which ethanol is employed to finely tune the density/coverage of sodium dodecyl sulfate (SDS) on nanotubes, and thus the interactions between SWCNTs and an allyl dextran-based gel. Incrementally increasing the ethanol content in a low-concentration SDS eluent leads to successive desorption of the different structure SWCNTs adsorbed on the gel, and to achieving multiple distinct (*n, m*) single-chirality species. The use of ethanol enables the working concentration of SDS to be reduced dramatically and also avoids the introduction of other surfactants or chemical reagents. More importantly, ethanol can be easily eliminated after separation. The ability of ethanol to tune the interactions between SWCNTs and the gel also gives a deeper insight into the separation mechanism of SWCNTs with gel chromatography.

1. Introduction

A population of single-chirality nanotubes with identical property is critical to fabricate high-performance single-wall carbon nanotubes (SWCNTs) based devices in various fields.[1–5] However, most of the current synthesis techniques of SWCNTs generally produce mixtures of different structures, making the devices difficult to reflect the intrinsic outstanding characteristics of SWCNTs. To overcome the limitation, scientists made great efforts to develop various post synthetic methods to separate SWCNTs on the basis of their structures.[6–16] All of these methods are capable of achieving the separation of metallic and semiconducting SWCNTs. Density gradient ultracentrifugation,[9,10] polymer wrapping,[11,12,13] DNA wrapping chromatography[14,15] and two-phase extraction[16] even allow researchers to isolate multiple distinct (*n, m*) single-chirality species. Nevertheless, these powerful and effective methods suffer from the drawbacks of high cost, low throughputs, or low purity. Moreover, these liquid processing methods involve two or more surfactants and even DNA/polymers, which are very difficult to remove after separation and affect the scientific research and technical applications of the separated nanotubes.

Recently, we developed a multicolumn gel chromatography to extract 13 distinct (*n, m*) species from HiPco-SWCNTs using an allyl dextran-based gel, which is thought as the most promising technique for industrial separation because of its low cost, simplicity and scalability.[17] In this technique, only a single surfactant of sodium dodecyl sulfate (SDS) is used as both the dispersant and eluent for SWCNTs, and the gel medium can be reused. Simply loading an excess of SDS-dispersed SWCNT aqueous solution to multi-stage gel columns leads to the sorting of SWCNTs based on structure across different columns from top to bottom with a gel interaction strength ranging from strongest to weakest. The adsorbed nanotubes on each gel column are then desorbed and collected using a 5-wt % SDS aqueous solution. We propose that the coverage and/or thickness of the SDS coating around nanotubes are the key factors for determining the interactions between SWCNTs and the gel. The difference in the interactions of distinct (*n, m*) SWCNTs with the gel deriving from various SDS coverage around them drives their structure separation.[17,18] With this technique, repeating the separation process, nevertheless, has to be performed to achieve single-chirality SWCNTs. More recently, several modified methods were developed to improve the separation efficiency, by using temperature,[18] pH[19,20] or salt[21] to enlarge the existing difference in the SDS coverage among different-structure nanotubes and to increase the SWCNT structure resolution of gel chromatography. However, the temperature-controlled technique needs a temperature-controlled system and a high-concentration SDS aqueous solution for desorption of the adsorbed nanotubes, while the introduction of acidic aqueous

---

[a] School of Materials Science and Engineering, Nanchang University, Nanchang 330031, China. E-mail: nqzhou@163.com
[b] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China. E-mail: liuhuaping@iphy.ac.cn
[c] Beijing Key Laboratory for Advanced Functional Materials and Structure Research, Beijing 100190, China
[d] Collaborative Innovation Centre of Quantum Matter, Beijing 100190, China

† † Electronic Supplementary Information (ESI) available: Figures S1-S13, additional discussion and experimental details. See DOI:10.1039/x0xx00000x

solution or salt would inevitably introduce additional impurities and even damage hydro-gels.

On the basis of the fact that ethanol could affect the critical micelle concentration (CMC) of SDS solution,[22–26] we developed an ethanol-assisted gel chromatography for the chirality separation of SWCNTs, in which ethanol was introduced to finely tune the SDS coatings around SWCNTs, and thus the interaction of SWCNTs with the gel. As the content of ethanol increases in the SWCNT dispersion, the adsorbability of semiconducting (S-) SWCNTs onto the gel decreases gradually in a species-selective manner. Specifically, the adsorbability of the S-SWCNTs with smaller C-C bond curvatures decreases earlier and greater than that of the S-SWCNTs with larger bond curvatures. Thus, by simply adjusting the ethanol content in the SDS-dispersed SWCNT solution or in a SDS eluent of 1-2 wt %, the chirality separation can be achieved. Clearly, this novel method enables the working concentration of SDS to be reduced dramatically than previously reported,[17,18] and does not require any additional materials or equipment except for ethanol. Furthermore, compared with the methods tuning by pH or salt, ethanol has no damage to SWCNTs or the gel, and can be removed more easily after separation.

2. Results and discussion

2.1. Effect of ethanol on the adsorbability of SWCNTs onto a gel column

To investigate the effect of ethanol on the adsorbability of SWCNTs onto the gel, 5-ml aliquots of HiPco-SWCNT dispersion with various ethanol contents and 2 wt % SDS were prepared and then loaded to a gel column packed with 4 ml of gel beads, respectively. The adsorbed nanotubes were eluted by a 5-wt % SDS aqueous solution and the volumes of the fractionally collected nanotubes were fixed at 2 ml. The optical absorption spectra for the adsorbed nanotubes are presented in Fig. 1a. With an increase in the ethanol content from 0 to 7% (v/v), the optical absorbance for the adsorbed nanotubes in near infrared region at longer wavelengths such as 1119 and 1173 nm attenuate more dramatically than those at shorter wavelengths (*e.g.* 873 and 976 nm), indicating this is a diameter-selective process (also see ESI, Fig. S1 and S2†). When the ethanol content in the SWCNT dispersion reaches 7% (v/v), only one main absorption peak at 976 nm in the spectrum is observed, which corresponds to the absorption of the E_{11} band-gap of the (6, 5) nanotubes, implying that the adsorbed nanotubes are highly enriched in (6, 5) nanotubes. With further increasing the ethanol content, the optical absorbance for (6, 5) nanotubes continuously decreases. When the ethanol content is beyond 10% (v/v), nearly no nanotubes could be detected in the adsorbed fraction (ESI Fig. S3†).

To more precisely describe the effect of ethanol on the adsorbability of SWCNTs onto the gel, we quantitatively evaluated the amount and diameter distribution of the adsorbed nanotubes as a function of ethanol contents, as shown in Fig. 1b and c. The evaluation method is similar to that reported previously.[17,18] PeakFit software was used to simulate the near-IR optical absorption spectra representing the individual (*n, m*) species with wavelengths from 800 to 1350 nm, as shown in Fig. S4a†. Since the volume of each collected fraction is the same, the amount of the adsorbed nanotubes could be represented by the sum of all the absorption peak areas in near-IR optical absorption spectra, and its relative amount is computed as the ratio of the amount of the adsorbed nanotubes at each ethanol content to that without ethanol addition. As shown in Fig. 1b, with an increase in the ethanol content from 0 to 7 % (v/v), the adsorbed nanotubes decrease by 90 %, indicating that the introduction of ethanol dramatically decreases the adsorbability of the nanotubes onto the gel. In order to describe the selective adsorption of different-structure SWCNTs under different contents of ethanol, the relative abundances of the (7, 6) (0.895 nm in diameter), (7, 5) (0.829 nm in diameter), and (6, 5) (0.757 nm in diameter) nanotubes in each adsorbed fraction were calculated by the relative peak intensities of their photoluminescence (PL) contours and the results were summarized in Fig. 1c (uncorrected for the chiral-dependent quantum yield). The corresponding PL contours were presented in ESI, Fig. S2†. As shown in Fig. 1c, an increase in the ethanol content from 0 to 7%

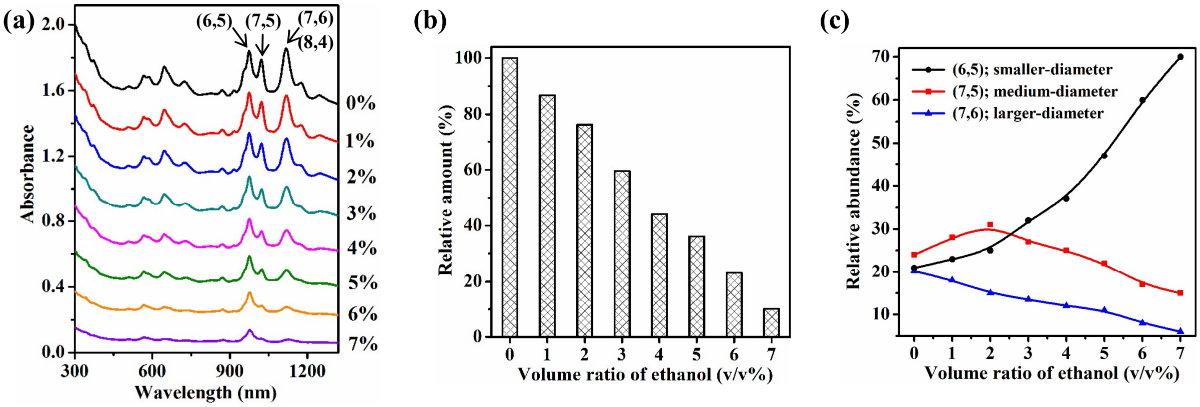


Fig. 1 Optical characterization and analysis of the adsorbed nanotubes onto the gel under different ethanol contents. (a) Optical absorption spectra. The spectra shift vertically for comparison. The ethanol contents are indicated beside each spectrum. (b) The relative amount of the adsorbed SWCNTs as a function of ethanol contents, which were evaluated by the absorption spectra in (a). (c) The relative abundances of the (6, 5); (7, 5); and (7, 6) species in the adsorbed SWCNT fractions as a function of ethanol contents, which were calculated based on the relative peak intensities of their PL contours presented in Fig. S2†.

(v/v) leads to three change trends for the different diameter nanotubes in their relative abundances: (i) the relative abundance of the (7, 6) SWCNTs with larger diameters decreases monotonously from 20.3 to 5.8%; (ii) that of the (7, 5) nanotubes with medium diameter increases initially and then decreases; and (iii) that of the (6, 5) nanotubes with smaller diameters increases monotonously from 20.9 to 70.1%. These results sufficiently indicate the introduction of ethanol to the SDS-dispersed nanotube solution leads to highly selective adsorption of different diameter nanotubes onto the gel by changing their adsorbability. A similar change trend for the relative abundances of different diameter nanotubes was further achieved by absorption spectra,[17, 18] in which the relative abundances of (7, 6) and (8, 4) nanotubes were calculated by the area of their superposed absorption peaks in near-infrared region (see ESI, Fig. S4b†) because their absorption peaks cannot be fully resolved by fitting. To further investigate the ethanol-dependent adsorbability of SWCNTs onto the gel, the cases of SWCNTs dispersed in 1 wt % SDS with various ethanol contents were also studied, and a similar result was achieved (ESI Fig. S5 and S6†).

2.2. Chirality separation by ethanol-assisted gel chromatography

As demonstrated above, increasing the ethanol content in a SDS-dispersed SWCNT solution reduces the adsorbability of SWCNTs onto the gel in a species-selective manner. When the ethanol content reaches 7% (v/v), the adsorbed nanotubes are highly enriched in (6, 5) species, achieving the separation of (6, 5) nanotubes from the initial SWCNT mixture. The separation of additional (*n, m*) species in the mixture of SWCNTs can be achieved by repeatedly tuning the ethanol contents in the flowing-through SWCNTs fractions from higher to lower and reloading them into the gel column. During each process, only the species having the adsorbability onto the gel could be adsorbed and thus sorted from the mixture of nanotubes. However, this is a tedious and inefficient process. To simplify the separation process, we propose that, if the interaction between the adsorbed nanotubes and gel could be tuned by ethanol, the adsorbed nanotubes can be selectively desorbed successively by incrementally increasing the ethanol content in a low-concentration SDS eluent, leading to high-efficiency chirality separation of SWCNTs.

To confirm the hypothesis, we designed an ethanol-assisted gel chromatography method, as illustrated in Fig. S7†. We applied a 2-ml aliquot of the parent SWCNT dispersion to a gel column packed with 12 ml of gel beads and washed away the unadsorbed nanotubes. The stepwise elution of the adsorbed nanotubes was performed by varying the ethanol content in a SDS eluent from lower to higher. As we know, when a SDS-dispersed SWCNT solution is applied to a gel column, the amount and types of the adsorbed nanotubes are inversely proportional to the SDS concentration.[27] Most of the S-SWCNTs in HiPco-SWCNT dispersion could be adsorbed under 1 wt % SDS.[18,27] On the other hand, the purities of the separated S-SWCNTs strongly depend on the chirality distribution of the starting materials.[28] Thereby, in order to enhance the resolution of the chirality separation, a preselection is necessary to reduce the types of the adsorbed species by adjusting the SDS concentration of the SWCNT dispersion from 2 wt % to 1.5 wt % and finally to 1 wt %. Specifically, the raw SWCNT mixture was initially dispersed in a 2-wt % SDS aqueous solution. After loading the SWCNT dispersion to the gel column, the stepwise elution of the adsorbed nanotubes was performed by the ethanol-contained SDS eluents, in which the SDS concentration was fixed at 2 wt % and the ethanol content was incrementally increasing from 2 to 10% (v/v). Next, the flow-through fraction was diluted to 1.5 wt % SDS for the second separation. At this stage, the adsorbed nanotubes were eluted with a series of 1.5-wt % SDS solutions containing various ethanol contents ranging from 2 to 8% (v/v). Similarly, the flow-through fraction with 1.5 wt % SDS was further diluted to 1 wt % SDS for the third process. To understand which species adsorbed at each SDS concentration, a parallel experiment was conducted, in which the adsorbed nanotubes were desorbed in one step by a SDS solution of 5 wt %.

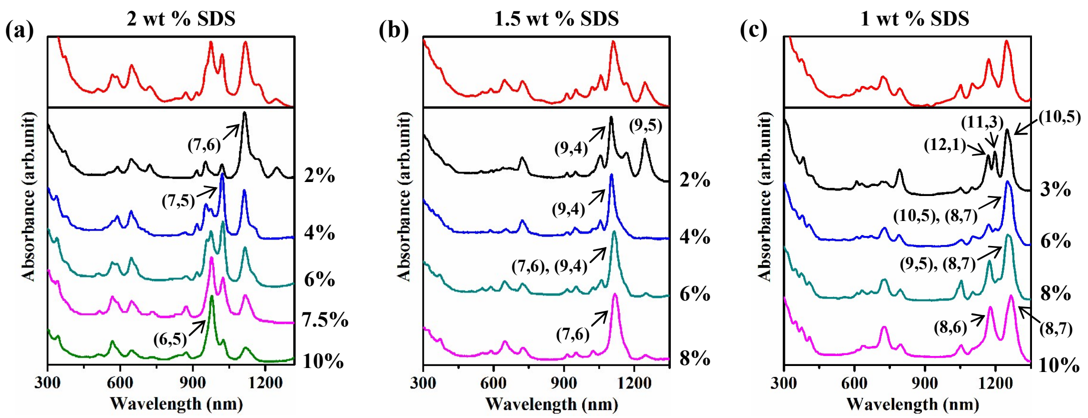


Fig. 2 Optical absorption analysis of the eluted nanotube fractions by the ethanol-contained SDS eluents with various ethanol contents from lower to higher. The SDS concentration in the ethanol-contained eluents is the same with those in the corresponding SWCNT dispersions: (a) 2 wt %, (b) 1.5 wt % and (c) 1 wt %. In (a)-(c), the top spectra correspond to the adsorbed nanotubes and the lower spectra represent the eluted fractions. The ethanol contents in the eluents are indicated beside each spectrum. All the spectra are normalized at S_{11} peaks (800-1300 nm) and offset for comparison.

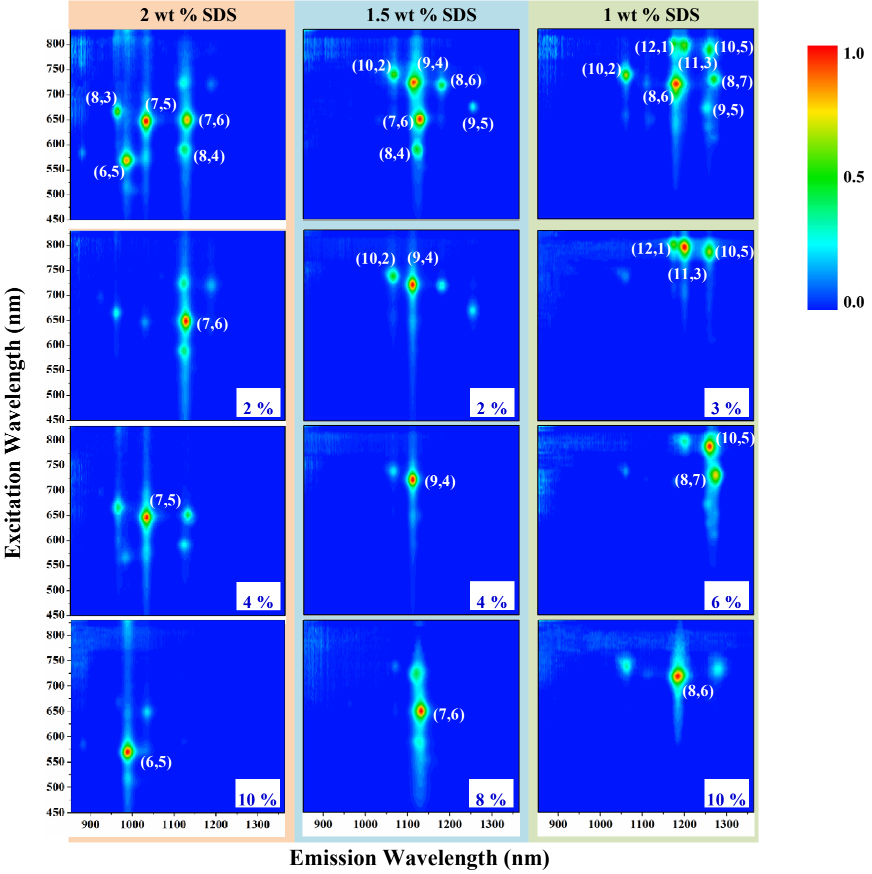


Fig. 3 Photoluminescence (PL) contours of the corresponding fractions in Fig. 2. The top one in each column represents the PL contour of the adsorbed nanotubes under 2 wt %, 1.5 wt % and 1 wt % SDS, respectively. The lower contours in each column represent several featured fractions collected by the stepwise elution. The ethanol contents in the eluents are indicated in the lower right corner on each spectrum.

The optical absorption spectra and PL contours for the adsorbed nanotubes under different SDS concentrations are presented in the top panels in Fig. 2 and 3, respectively. Compared with the PL map of the raw HiPco-SWCNTs (ESI Fig. S8a†), it is evident that the preselection results in a narrower chirality distribution of each adsorbed fraction. The collected fractions by the stepwise elution were also characterized, as shown in the lower panels in Fig. 2 and 3 (also see ESI, Fig. S8 and S9†). These results clearly show that the chirality separation of the adsorbed nanotubes was further achieved by the selective desorption. Especially, near single-chiral (6, 5), (7, 6) and (9, 4) nanotubes were obtained.

To understand the structure selectivity of nanotubes during the stepwise elution, we analyze the relationship between the elution order of distinct (*n, m*) species and their chiral angles (θ), diameters (D_t), and smallest C-C bond curvature radii (R_c, $R_c = D_t / 2 \cos^2 (30-θ)$)[17]. As shown in Fig. 4, the smallest C-C bond curvature radii of

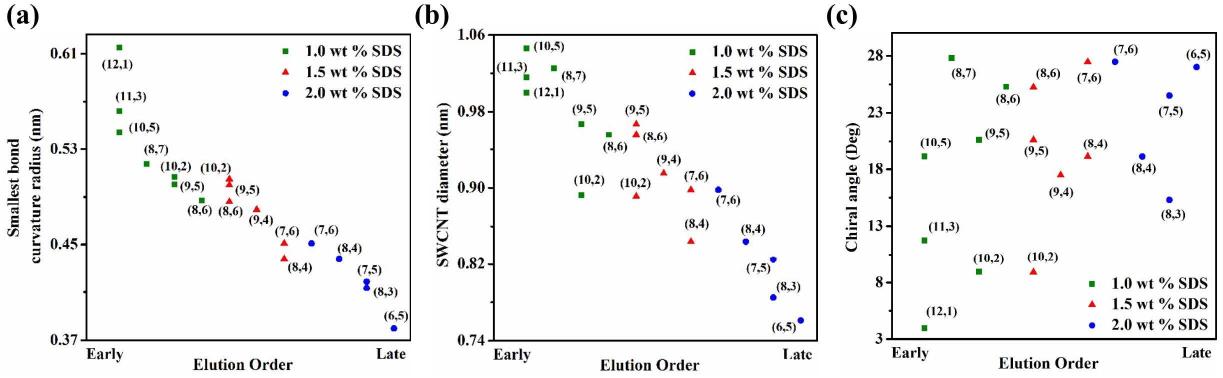


Fig. 4 The relationship between the elution order of (*n, m*) nanotubes and their physical structures. (a) Smallest C-C bond curvature radii. (b) Diameters. (c) Chiral angles.

distinct (*n, m*) nanotubes exhibit a smoothest change along their elution order under each SDS concentration among 2 wt %, 1.5 wt % and 1 wt %, indicating that the structure selectivity of nanotubes is most strongly dependent on their largest C-C bond curvatures. In contrast, the chiral angles have a weakest effect on their sorting process because of their scatter distribution along the elution order (Fig. 4c). This result is in agreement with our previous work.[17] In addition, the structure selectivity of nanotubes during the preselection is also very obvious (Fig. 4a and b). The nanotubes with smaller diameters or C-C bond curvature radii can be adsorbed onto the gel even under higher SDS concentrations, exhibiting stronger interaction strength with the gel.

To improve the chirality purity, we should further reduce the types of the adsorbed nanotubes onto the gel column by controlling the SDS concentration in the preselection process. For this, the raw SWCNTs were initially dispersed in a 2.5-wt % SDS solution. The as-prepared SWCNT dispersion was applied to a gel column and the stepwise elution was performed by incrementally increasing the ethanol contents in a 2.5-wt % SDS eluent. For comparison, the adsorbed nanotubes were eluted with a SDS solution of 5 wt %. As shown in Fig. 5a and S10a†, the adsorbed nanotubes were enriched in (6, 5) nanotubes. Through the stepwise elution, several high-purity (6, 5) nanotube fractions were easily achieved, among which the highest purity could reach about 90% at the third elution step using the eluent containing 6 % (v/v) ethanol (Fig. 5a and c). The flow-through fraction was diluted to 2 wt % SDS for the second separation. At this stage, the (7, 6) and (7, 5) nanotubes with higher purity were achieved by the stepwise elution using 2-wt % SDS eluents containing 2 % (v/v) and 8 % (v/v) ethanol respectively (Fig. 5b, d and e), because of a narrower chirality distribution of the adsorbed nanotubes (Fig. 5b and S10b†) compared with that in Fig. 2a and 3. On the basis of these results, we can expect that more types of high-purity single-chirality nanotubes could be achieved by precisely controlling the SDS concentration in a SWCNT dispersion and/or using other methods, such as overloading[17] and temperature-controlled method[18] to further reduce the types of the nanotubes adsorbed onto the gel in the preselection process. Besides, using an appropriate gradient concentration of ethanol in the SDS eluents in the stepwise elution process might also improve the separation purity greatly.

2.3. A novel ethanol-assisted elution method

In the previous works,[17,18,27,28] an aqueous solution of 5 wt % SDS has to be used as the eluent for one-step desorption of the adsorbed nanotubes. Since the introduction of ethanol into a low-concentration SDS (1-2 wt %) aqueous solution is capable of desorbing the adsorbed nanotubes from the gel, a mixture aqueous solution of ethanol and SDS might serve as an alternative eluent, which would reduce the separation cost dramatically. More importantly, ethanol can be easily removed and has little negative effect on the properties of the separated nanotubes.

To explore the desorption behaviours of the adsorbed nanotubes by the ethanol-contained SDS eluent, the following experiments have been performed. Two 0.3-ml aliquots of the parent SWCNT/2 wt % SDS dispersion were loaded to double gel columns. Each of them was packed with 4 ml of gel beads. The adsorbed nanotubes

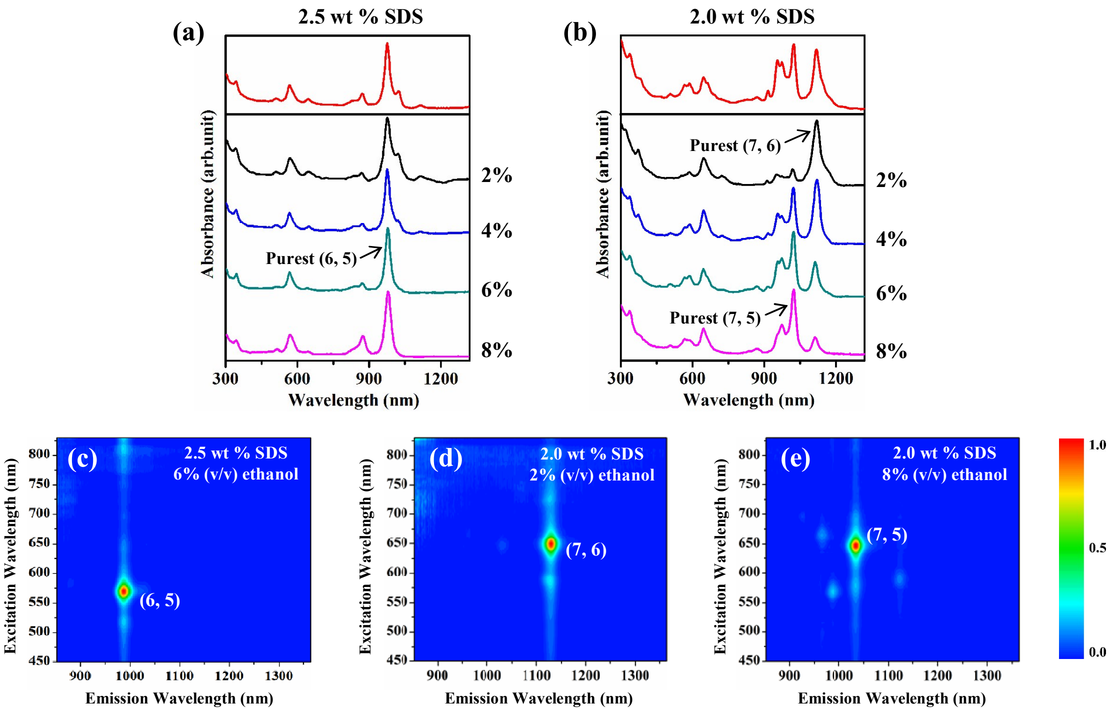
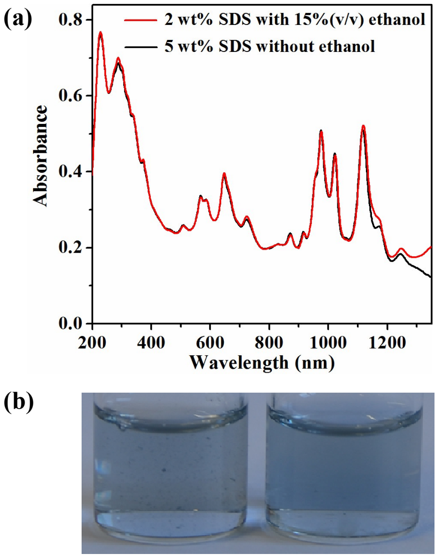


Fig. 5 Optical characterization of the separated nanotubes. (a-b) Optical absorption spectra. The top spectra correspond to the adsorbed nanotubes at 2.5 wt % SDS and 2 wt % SDS, respectively. The lower spectra represent the fractions eluted by the 2.5 wt % SDS eluents or 2 wt % SDS eluents containing various ethanol contents. All the spectra are normalized at S_{11} peaks and shift vertically for comparison. (c-e) PL contours of the purest (6, 5), (7, 5) and (7, 6) fractions among all the eluted fractions in (a) and (b).

in one column were eluted by a 2-wt % SDS eluent with 15% (v/v) ethanol while those in another column were eluted by an aqueous solution of 5 wt % SDS. As shown in Fig. 6a, the absorption spectra for the two collected nanotube fractions well overlap. The case of SWCNT dispersion in 1 wt % SDS was also investigated. A similar result was obtained (ESI Fig. S12†). These results indicate that the novel ethanol-contained SDS eluent can be used to replace the eluent of 5 wt % SDS.

Additionally, we found that the nanotube fractions collected with the ethanol-contained SDS eluent were more stable, in which no obvious SWCNT bundles were present after standing for 60 days. By contrast, the nanotubes eluted and collected by 5-wt % SDS eluent started to aggregate and form visible bundles after standing for 15 days, and as time went on, more and more bundles appeared. This difference can be seen clearly from their photographs in Fig. 6b. The stability for the eluted nanotubes was further confirmed via centrifugation (ESI Fig. S13†). The reason for the higher stability of the nanotubes collected by the ethanol-contained SDS eluent is still unclear. We believe this is likely related to the SDS concentration. Sun *et al.* reported that 1 wt % SDS is the optimum concentration for stabilizing SWCNT dispersion.[29] The SDS concentration in the ethanol-contained SDS eluent is closer to the optimum one and the corresponding SWCNT solution should be more stable.



5 wt% SDS Ethanol + 2 wt% SDS

Fig. 6 Comparison of the two nanotube fractions eluted by an ethanol-contained SDS eluents and a 5-wt % SDS solution. (a) Optical absorption spectra. The components of each eluent are indicated. (b) Photographs of the eluted fractions after standing for 60 days. Left: 5 wt % SDS; Right: ethanol-contained eluent.

2.4. Possible mechanism for the chirality separation of SWCNTs by the ethanol-assisted gel chromatography

As demonstrated in our previous works,[17,18] the SDS coating around the nanotube surface determines the interaction of nanotubes and the gel. An increase in the coverage and/or thickness of the SDS coating on the nanotubes would lead to a decrease in their interaction with the gel. Here, because the addition of ethanol similarly leads to a selective decrease in the adsorbability of the SDS-dispersed nanotubes onto the gel, an increase in the ethanol content most likely induces the condensation of additional SDS molecules onto the nanotube surfaces in a selective manner and thus the formation of higher density of SDS coating.

According to several studies in colloidal science about the influence of ethanol on the micellization of SDS solution,[22-26] the introduction of ethanol into a SDS aqueous solution would decrease the CMC of SDS in the case of less than 15% (v/v) of ethanol, and subsequently increase the CMC with further increasing the ethanol content to higher than 15% (v/v). Specifically, an increase in the content of non-ionic ethanol dilutes the surface charge density in the palisade layer, thereby favouring the micellization and decreasing the CMC of SDS, which is defined as the cosurfactant effect and predominant under low ethanol contents. In contrast, when the ethanol content is high enough, a further increase would enhance the solubility of SDS considerably and thus increase its CMC, which is called as the cosolvent effect.

In the present work, because the ethanol content in either SWCNT/SDS dispersions (section 2.1) or the SDS eluents used in the stepwise elution for the chirality separation (section 2.2), is lower than 15% (v/v), the cosurfactant effect is dominant. Increasing the ethanol content would enhance the micellization of SDS molecules, causing additional SDS micelles to aggregate on the nanotube surfaces and forming higher SDS coverage around the SWCNTs, similar to the effect of increasing the SDS concentration, which decreases the interaction between SWCNTs and gel. Moreover, as shown in Fig. 1 and 4a, the decrease in the interaction between distinct (*n, m*) nanotubes and the gel, caused by increasing the ethanol content, is strongly dependent on the smallest C-C bond curvature radii (or diameters), suggesting that the bond curvature radii affect the condensation of SDS micelles and thus the density of the SDS coatings on the nanotube surfaces. Because an SDS molecule wrapping a larger-diameter SWCNT with a small bond curvature encounters a smaller energetic barrier, the SDS molecules therefore prefer to adsorb onto them.[18,30] An increase in the ethanol content enhances the selective adsorption of SDS micelles based on the SWCNT diameters, enlarging the differences in the coverage and/or thickness of the SDS coatings among various nanotubes and resulting in a more rapid decrease in the adsorbability of the larger-diameter nanotubes onto the gel (Fig. 1), and thus their earlier and faster desorption from the gel than the smaller-diameter species during the stepwise elution (Fig. 4).

As mentioned above, when the ethanol content in a SDS solution is high enough, the cosolvent effect outweighs the cosurfactant effect, resulting in an increase in the solubility of SDS with the ethanol content.[22,25,26] Thus, we can imagine that increasing the ethanol content in a SDS-dispersed SWCNT solution to higher than a certain value would lead to a decrease in the SDS coverage on the nanotubes due to a dramatic increase in the solubility of SDS. This inevitably causes a sharp increase in the interaction of the nanotubes with the gel and even the aggregation of SWCNTs. To confirm this prediction, the ethanol-dependent adsorbability of the SDS-wrapped SWCNTs on the gel was further studied by increasing the ethanol content to higher than 15% (v/v). After loading the SWCNT/2 wt % SDS dispersion containing 18% (v/v) ethanol or greater to a gel column, the colour of the column top turned into black, and the thickness of the colour increased with increasing the ethanol content, indicating that the amount of the adsorbed nanotubes increased. However, the adsorbed nanotubes was unable to be eluted even by a solution of 0.5 wt % DOC, suggesting that this adsorption was irreversible. Furthermore, we directly observed that the dispersed nanotubes aggregated in the form of algae-like structures with an increase in the ethanol content to 25% (v/v) in a SWCNT dispersion. This result is well consistent with our predictions. Therefore, the change trend in the adsorbability of SWCNTs onto the gel with increasing the ethanol content is well coincident with the CMC change of SDS,[22-25] evidencing that the driving force of the ethanol-tuning interaction between SWCNTs and the gel derives from the CMC change of SDS. Actually, chirality selectivity was previously achieved with gel chromatography by introducing another alcohol, 1-dodecanol, into SWCNT dispersion or SDS eluents.[19] However, the use of ethanol in the present work has more advantages such as low cost, easy removal and no damage to nanotubes. Besides, our present model can also be used to clarify the structure sorting mechanism of nanotubes by adding 1-dodecanol because 1-dodecanol can decrease the CMC of SDS,[22,31] similar to the effect of ethanol on the CMC of SDS.

3. Conclusions

We developed an ethanol-assisted gel chromatography to separate single-chirality nanotubes from a Hipco-SWCNT mixture, in which ethanol was exploited to finely tune the SDS coverage around the nanotubes and thus the interactions between nanotubes and the gel. Compared with the separation techniques by introducing acidic solutions or salt, ethanol has no negative effect on SWCNTs or the gel and the chirality sorting of SWCNTs can be achieved in a cost-effective way by simply controlling the ethanol content. The ability of ethanol tuning the interactions between nanotubes and the gel further confirms the separation mechanism that the different coverage degrees of the SDS coatings around different SWCNTs are the driving force for their chirality separation. Additionally, ethanol enables a low-concentration SDS solution to have a strong desorption ability of nanotubes from the gel. An ethanol-contained low-concentration SDS solution can thus serves as an alternative eluent for high-concentration SDS solution or other surfactant solutions, which not only cuts down the separation cost but also reduces/avoids the negative effects of high-concentration SDS or other surfactants/polymers on the separated nanotubes. The present advances have great significance for studying the intrinsic properties of SWCNTs and their technical applications in optics, electronics, and optoelectronics.

4. Experimental

HiPco-SWCNTs (R1-794, 1.0±0.3 nm in diameter) purchased from NanoIntegris Inc. were used as the starting material. To prepare the SWCNT dispersion, 20 mg of SWCNTs were dispersed in 20 ml of purified water with 2 wt % SDS (99%, Sigma-Aldrich) using a tip-type ultrasonic homogenizer (Sonifire 450D, Branson) for 2 h at 30% power. During the sonication, the sample was immersed in a water bath at 15 °C to prevent heating. Then the resulting dispersion was centrifuged at 210 000 × g for 30 min using an ultracentrifuge (S50A, Hitachi CS150FNX) to remove nanotube bundles and impurities. The upper 80% of the supernatant was collected as the parent SWCNT dispersion.

To explore the effect of ethanol on the adsorbability of SWCNTs onto the gel, ethanol contents in 5-ml aliquots of SWCNT dispersion were varied from 0 to 25% (v/v) by adding pure ethanol (analytical grade, Beijing Tong Guang Fine Chemicals Corp.) to 0.5-ml aliquots of the parent SWCNT dispersion. The SDS concentration was fixed at 2 wt %. The as-prepared SWCNT dispersions were left to stand overnight to achieve equilibrium. A gel column was prepared by filling 4 ml of allyl dextran-based gel beads (Sephacryl S-200 HR, GE Healthcare) into a 10-ml medical syringe, and equilibrated by a 2-wt % SDS solution containing certain content of ethanol. Then, the corresponding SWCNT dispersion with the same ethanol content was applied to the column and the unadsorbed nanotubes were washed away sufficiently by the corresponding ethanol-contained SDS solution. To eliminate the effect of various ethanol contents on the measured spectra, a 2-wt % SDS aqueous solution (without ethanol) was poured to the column to remove the remaining ethanol. Finally, the adsorbed SWCNTs were eluted by a 5-wt % SDS aqueous solution. The effect of ethanol on the adsorbability of SWCNTs dispersed in 1wt % SDS was also conducted similarly.

For the chirality sorting, a gel column was prepared by filling 12 ml of gel beads into a 50-ml syringe. After equilibration with a 2-wt % SDS aqueous solution, a 2-ml aliquot of the parent SWCNT dispersion (without ethanol) was loaded to the column. The unadsorbed nanotubes were washed away using a 2-wt % SDS aqueous solution and collected as the flow-through fraction. The stepwise elution was performed for desorption of the nanotubes adsorbed on the gel by incrementally increasing the ethanol content in a 2-wt % SDS aqueous eluent from 2 to 10% (v/v). At each concentration of ethanol, adequate eluent was injected until no nanotubes could be detected in the collected eluent. After that, the flow-through fraction was diluted to 1.5 wt % SDS by pure H_2O for the second separation. At this stage, the adsorbed nanotubes were similarly eluted by varying the ethanol content in a 1.5-wt % SDS eluent ranging from 2 to 8% (v/v). Finally, the flow-through fraction in the case of 1.5 wt % SDS was further diluted to 1 wt % SDS for the third separation using a similar stepwise elution process.

Optical absorption spectra were recorded from 200 to 1350 nm utilizing an UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu). The photoluminescence (PL) contour map of each sample was measured using a spectrofluorometer (Horiba, Nanolog) equipped with a liquid nitrogen-cooled InGaAs detector and a 350W xenon lamp as excitation source. Notably, before the spectroscopic characterization, the pH value of each sample was adjusted to 8 by adding NaOH solution with several microliters, to suppress the bleaching effect.[32]

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 51472264, 51361022). H. L. thanks support by the Recruitment Program of Global Youth Experts and the "100 talents project" of CAS.

Notes and references

1. D. H. Zhang, K. Ryu, X. L. Liu, E. Polikarpov, J. Ly, M. E. Tompson and C. W. Zhou, *Nano Lett.*, 2006, **6**, 1880−1886.
2. L. J. Yang, S. Wang, Q. S. Zeng, Z. Y. Zhang, T. Pei, Y. Li and L. M. Peng, *Nat. Photonics*, 2011, **5**, 673–677.
3. S. Mao, S. M. Cui, K. H. Yu, Z. H. Wen, G. H. Lu and J. H. Chen, *Nanoscale*, 2012, **4**, 1275-1279.
4. M. Engel, J. P. Small, M. Steiner, M. Freitag, A. A. Green, M. C. Hersam and P. Avouris, *ACS Nano*, 2008, **2**, 2445–2452.
5. R. M. Jain, R. Howden, K. Tvrdy, S. Shimizu, A. J. Hilmer, T. P. McNicholas, K. K. Gleason and M. S. Strano, *Adv. Mater.*, 2012, **24**, 4436–4439.
6. R. Krupke, F. Hennrich, H. V. Löhneysen and M. M. Kappes, *Science*, 2003, **301**, 344–347.
7. S. Park, H. W. Lee, H. Wang, S. Selvarasah, M. R. Dokmeci, Y. J. Park, S. N. Cha, J. M. Kim and Z. Bao, *ACS Nano*, 2012, **6**, 2487–2496.
8. Y. Miyata, T. Kawai, Y. Miyamoto, K. Yanagi, Y. Maniwa and H. Kataura, *J. Phys. Chem. C*, 2007, **111**, 9671–9677.
9. M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp and M. C. Hersam, *Nat. Nanotechnol.*, 2006, **1**, 60–65.
10. S. Ghosh, S. M. Bachilo and R. B. Weisman, *Nat. Nanotechnol.*, 2010, **5**, 443–450.
11. F. Chen, B. Wang, Y. Chen and L. J. Li, *Nano Lett.*, 2007, **7**, 3013–3017.
12. H. Ozawa, T. Fujigaya, Y. Niidome, N. Hotta, M. Fujiki and N. Nakashima, *J. Am. Chem. Soc.*, 2011, **133**, 2651–2657.
13. M. Tange, T. Okazaki and S. Iijima, *J. Am. Chem. Soc.*, 2011, **133**, 11908-11911.
14. M. Zheng and E. D. Semke, *J. Am. Chem. Soc.*, 2007, **129**, 6084–6085.
15. X. Tu, S. Manohr, A. Jagota and M. Zheng, *Nature*, 2009, **460**, 250–253.
16. J. A. Fagan, C. Y. Khripin, C. A. Silvera Batista, J. R. Simpson, E. H. Hároz, A. R. Hight Walker and M. Zheng, *Adv. Mater.*, 2014, **26**, 2800–2804.
17. H. P. Liu, D. Nishide, T. Tanaka and H. Kataura, *Nat. Commun.*, 2011, **2**, 309.
18. H. P. Liu, T. Tanaka, Y. Urabe and H. Kataura, *Nano Lett.*, 2013, **13**, 1996–2003.
19. B. S. Flavel, M. M. Kappes, R. Krupke and F. Hennrich, *ACS Nano*, 2013, **7**, 3557–3564.
20. B. S. Flavel, K. E. Moore, M. Pfohl, M. M. Kappes and F. Hennrich, *ACS Nano*, 2014, **8**, 1817–1826.
21. A. Hirano, T. Tanaka, Y. Urabe and H. Kataura, *ACS Nano*, 2013, **7**, 10285–10295.
22. R. Zana, *Adv. Colloid Interface Sci.*, 1995, **57**, 1–64.
23. P. C. Griffiths, N. Hirst, A. Paul, S. M. King, R. K. Heenan and R. Farley, *Langmuir*, 2004, **20**, 6904–6913.
24. S. Javadian, H. Gharibi, B. Sohrabi, H. Bijanzadeh, M. A. Safarpour and R. Behjatmanesh-Ardakani, *J. Mol. Liq.*, 2008, **137**, 74–79.
25. S. Hitoshi, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1470–1474.
26. A. A. Rafati, H. Gharibi and M. Rezaie-Sameti, *J. Mol. Liq.*, 2004, **111**, 109–116.
27. A. J. Blanch, J. S. Quinton and J. G. Shapter, *Carbon*, 2013, **60**, 471–480.
28. H. P. Liu, T. Tanaka and H. Kataura, *Phys. Status Solidi B*, 2011, **248**, 2524–2527.
29. Z. Sun, V. Nicolosi, D. Rickard, S. D. Bergin, D. Aherne, and J. N. Coleman, *J. Phys. Chem. C*, 2008, **112**, 10692–10699.
30. N. R. Tummala and A. Striolo, *ACS Nano*, 2009, **3**, 595−602.
31. K. Shirahama and T. Kashiwabara, *J. Colloid Interface Sci.*, 1971, **36**, 65–70.
32. G. Dukovic, B. E. White, Z. Y. Zhou, F. Wang, S. Jockusch, M. L. Steigerwald, T. F. Heinz, R. A. Friesner, N. J. Turro and L. E. Brus, *J. Am. Chem. Soc.*, 2004, **126**, 15269–15276.