

Fractionation of Single Wall Carbon Nanotubes by Length Using Cross Flow Filtration Method

Shigekazu Ohmori,[†] Takeshi Saito,^{†,*} Bikau Shukla,[†] Motoo Yumura,[†] and Sumio Iijima[†]

[†]Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Ibaraki, 305-8565 Japan, and [†]PRESTO, Japan Science and Technology Agency, Tokyo, 102-0075 Japan

ABSTRACT A novel system for fractionating single wall carbon nanotubes (SWCNTs) by length *via* a three-step cross-flow filtration has been developed in which three membrane filters of different pore sizes, 1.0, 0.45, and 0.2 μm , were used. SWCNTs dispersed in water with the help of sodium carboxymethylcellulose (CMC) detergents were successfully sorted into four samples, and the atomic force microscopy (AFM) observation of those samples confirmed that their length distribution peaks are within the expected ranges from pore sizes of used filters. However, the result of the similar filtration process using a different detergent, sodium dodecylbenzenesulfonate (SDBS), showed no pronounced correlation between the length distribution of SWCNTs and the pore size. The observed difference in the sorting phenomena caused by the detergent type suggests that the permeation property depends on the complex structure resulting from the dispersed SWCNTs and detergent molecules.

KEYWORDS: length fractionation · carbon nanotube · cross-flow filtration · sodium carboxymethylcellulose · sodium dodecylbenzenesulfonate · atomic force microscopy

Single wall carbon nanotubes (SWCNTs) are one of the most promising materials for the post silicon electronic applications because of their excellent electronic properties based on their chemical stability and mechanical strength.^{1–3} It is well-known that electronic properties of SWCNTs differ with their structural characteristics, such as, diameter, chirality, length, and so on.^{4–9} Especially the length of SWCNTs is important for applying to electronic devices with SWCNT interconnection networks of percolation.^{10,11} Controlled length with higher degree of homogeneity will produce the better and even performance of devices such as transparent conductive films and thin film transistors, because the electronic transport properties of such devices depend on the sum of contact resistances in each carrier pathways. Beside this, it has been reported that the length of SWCNTs can also critically affect their dispersing and optical (spectroscopic) properties.^{7–9,12,13} Thus, sorting of

SWCNTs by length is of great importance for both the fundamental understanding of their properties as well as for their applications.

As far as authors know, some techniques for sorting of SWCNTs by length, such as, size exclusion chromatography (SEC),^{14–16} centrifugation techniques,^{17,18} electrophoresis,^{19,20} and flow field-flow fractionation,^{21,22} have been reported to date. The former two techniques possess much more excellent fractionation precision than the latter ones, although the applicable length range was limited to a quite shorter range, typically less than 0.6 μm . In the case of the latter two techniques, in spite of their potential for wider length range than SEC, they suffered from the problem of aggregation of SWCNTs.^{19,22} Moreover, all these previous methods generally suffered from low throughput in their batch process. Therefore, developing an efficient method of sorting SWCNTs by length is still in demand for their applications.

RESULTS AND DISCUSSION

Considering the necessity of a technique having higher potential with greater throughput, here we propose a novel and scalable system that involves multistep cross-flow filtration through membrane filters of different pore sizes, as shown in Figure 1a,b. Briefly, in this system, at first the source suspension of SWCNTs was separated to retentate and permeate by the cross-flow filtration (Figure 1b). The permeate so obtained was reused as a source suspension for the next filtration step after changing the membrane filters of different pore sizes. By repeating similar procedures, the SWCNT suspension was separated into

*Address correspondence to takeshi-saito@aist.go.jp

Received for review January 21, 2010 and accepted June 1, 2010.

Published online June 7, 2010.
10.1021/nn100124v

© 2010 American Chemical Society

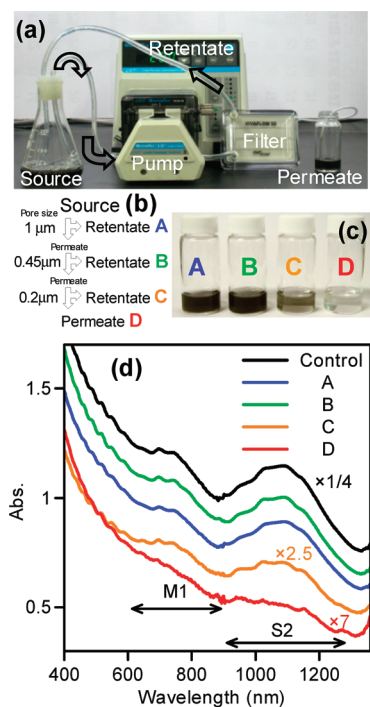


Figure 1. Photo image of the cross-flow filtration system (a), a schematic depiction of the three-step fractionation processes (b), sorted samples A–D (c), and their optical absorption spectra with that of the source suspension as a control (d).

four samples, that is, three retentates and one permeate of the last step, as shown in Figure 1b. Three different filter membranes of pore sizes, 1.0, 0.45, and 0.2 μm , were adopted in these three steps of filtration procedures. To understand the effect of dispersant on the length sorting phenomena, two detergents, CMC and SDBS were examined. Figure 1c shows the photographic images of the resulting fractionated samples A–D, separated from the CMC suspension. A–C are the retentates of filtrations with membranes of 1.0, 0.45, and 0.2 μm pore size, respectively, and D is the permeate of the last step. On the basis of the differences in

colors of A–D (Figure 1c), qualitatively it can be imagined that A and B contain greater amounts of SWCNTs than that of C and D. For the qualitative and quantitative analyses, especially to estimate the filtration efficiency, optical absorption spectra of those samples were measured in the wavelength range of 400–1350 nm, as plotted in Figure 1d. Rather weak profiles of C and D, because of their lower concentrations, are magnified 2.5 and 7 times. For comparison, the absorption spectrum of the source suspension is also shown as a control with the reduced intensity to 1/4. From the mean diameter of the used SWCNT sample, observed absorption peaks were attributed to the second interband transition of semiconducting SWCNTs (S2) and the first interband transition of metallic SWCNTs (M1) of electronic transitions,²³ as denoted in Figure 1d. It clearly shows that the shapes of absorption spectra of A–C are approximately consistent with the control. In the case of D, peak positions of S2 and M1 seem to be similar to others, although the spectrum feature is less resolved due to the reduced contents of SWCNTs. This qualitative comparison suggests that the effect of this fractionation process on the diameter distribution and the metal/semiconductor ratio is negligible.

On the basis of well-known quantitative correlation between the absorption intensity and the content of SWCNTs in their suspension,^{23,24} the relative concentrations of SWCNTs (C_{sample}) against the control can be derived from the observed absorption profiles of A–D by the following equation:

$$C_{\text{sample}} = \frac{\overline{I_{\text{sample}}(\lambda)}}{\overline{I_{\text{control}}(\lambda)}} \quad (1)$$

where I is absorption intensity, and the upper bar indicates the average of the component as a function of wavelength λ through the whole measured range of 400–1350 nm. The fractionation efficiency (P_{sample}) in each step is defined as the ratio of the content of

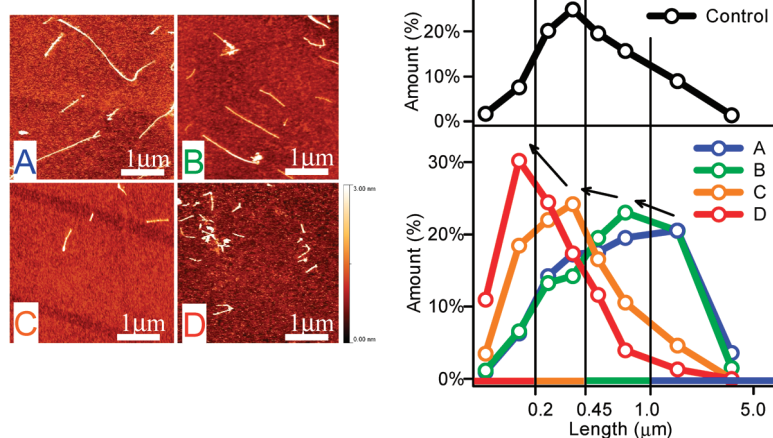


Figure 2. Typical topographic AFM images (left) and length distribution profiles (right) of SWCNTs in samples A–D. The length distribution of the source suspension dispersed by CMC is also plotted as a control.

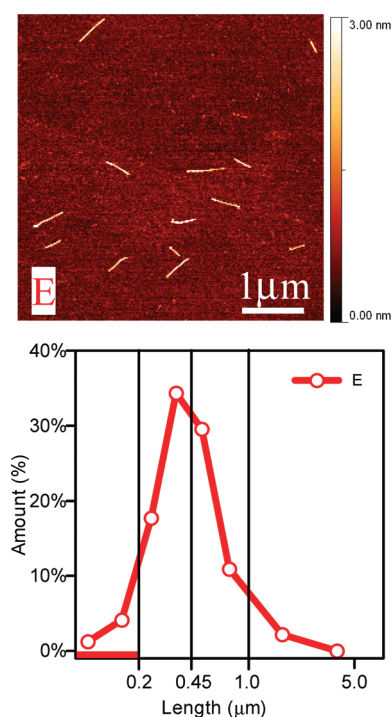


Figure 3. Typical topographic AFM image (left) and the length distribution profile (right) of SWCNTs in sample E.

SWCNTs in the fractionated suspension to that in the control and it can be expressed as follows:

$$P_{\text{sample}} = C_{\text{sample}} \cdot \frac{V_{\text{sample}}}{V_{\text{control}}} \times 100 \quad (2)$$

where V is the volume of suspension. From eq 2, the fractionation efficiency with one standard deviation in each step was calculated and the values obtained are as follows: A, $29 \pm 0.5\%$; B, $33 \pm 0.3\%$; C, $10 \pm 0.2\%$; and D, $2.9 \pm 0.5\%$. It should be noted that the total amounts

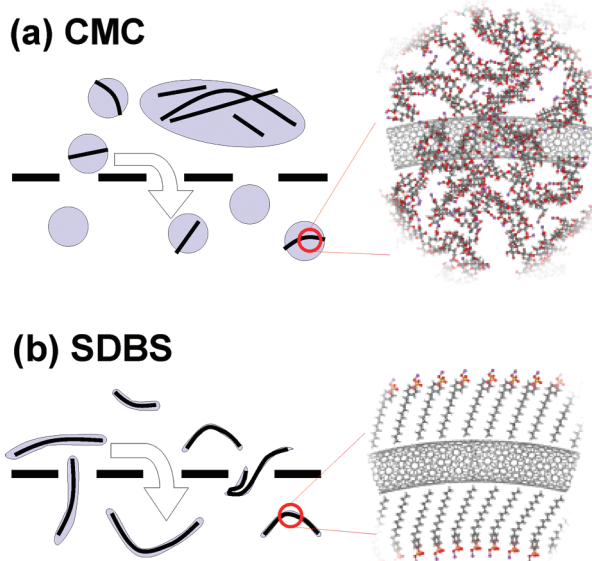


Figure 4. Possible mechanism of the difference between SWCNT suspensions dispersed by detergents CMC (a) and SDBS (b) in filtration. The filtration result can be changed by the flexibility of the complex structure of detergent molecules and SWCNTs.

of SWCNTs fractionated by these processes was about 75% from the summation of all P values. In other words, 25% of SWCNTs in the source suspension were lost in these processes, probably due to aggregation on filter membranes and inside of the TYGON tubes.

Figure 2 shows typical AFM topographic images of separated samples A–D. From the analysis of these images, in general, the height values of individual SWCNTs were found to be less than 3 nm, indicating that SWCNTs were dispersed into debundled or a few bundled ones. Length distribution profiles of A–D and the source suspension (control) from AFM measurements have been plotted in Figure 2. Note that these distribution data have been expressed as the percentage of measured counts in each sample, and that horizontal axis is scaled as log 10. It was found that length distribution peaks in profiles of four separated samples agree with the expected ranges from pore sizes of used filters. In B–D, more than 41% of SWCNTs are in the expected range supporting the greater potentiality of the fractionation process. The observed trend of sharpening in length distribution is reasonable, because the time taken for the fractionation of each succeeding fractions A–D is consequently longer following the fractionation proceeding.

To investigate the impact of the detergent type, the similar experimental procedures of fractionation were carried out for a SWCNT suspension prepared in SDBS solution that has been frequently used for dispersing them until now. Surprisingly, the completely different results were obtained compared to CMC. The total source suspension was permeated through all filters without remaining retentate, while the considerable amount of aggregates of SWCNTs were observed on filter membranes. As a final result, only 7% of SWCNTs were collected as a permeate sample labeled E. A typical AFM image and the length distribution profiles of E are presented in Figure 3. The profiles in Figure 3 clearly indicate that the length distribution of E is approximately the same as that of the control shown in Figure 2 by contrast. It means most of SWCNTs were longer than the pore size of the last filter ($0.2 \mu\text{m}$), although the proportion of SWCNTs longer than $1 \mu\text{m}$ were typically decreased. This relatively sharp distribution of E compared to that of the control suggests that longer SWCNTs might be trapped on used filters prior to shorter ones, resulting in aggregation. The main cause of this failure of the length sorting with SDBS suspension can be better explained on the basis of the analogy of SDBS to a similar type of detergent, sodium dodecanesulfonate (SDS). Similarly to SDS,^{25,26} SWCNTs should be covered with the monolayer of SDBS molecules called SDBS micelles that possess enough aspect ratio to pass through even smaller pores than their size. In addition, the reason behind the considerable aggregation of SWCNTs on the filter membrane is probably due to the removal of detergent molecules from

the SWCNTs' surface by the turbulence in the filtration system. A similar phenomena of aggregation was observed by Abatemarco *et al.*²⁷ in their work on cross-flow filtration of MWCNTs/SDS suspension, even though their result shows low or negative correlation between the average lengths of MWCNTs and pore sizes of filter membranes.

On the other hand, in the case of CMC, the successful sorting of SWCNTs by length must be due to the lower aspect ratio of their micelles. The origin of such a lower aspect ratio of CMC micelles is expected to be a long polymer chain (degree of polymerization ~ 400) with the high molecular weight (~ 90 kDa) of CMC. From this ability, it can wrap SWCNTs and leave them embedded in the matrix of the CMC polymer, which hopefully decreases the aspect ratio of their micelles, enabling them to be sorted by size. In other words, the permeation property of the dispersants, consisting of SWCNTs and detergent molecules, depends on their resulting complex structure, as illustrated in Figure 4. In addition, such a complex structure can also cause the difference in the aggregation property of SWCNTs ob-

served in the present study. Thus, it can be concluded that CMC is a suitable detergent for this fractionation system rather than the detergents that are generally used, such as SDBS and SDS.

In conclusion, a novel length fractionation system of SWCNTs with the multistep cross-flow filtration technique using three membrane filters of different pore sizes, 1.0, 0.45, and 0.2 μm , has been developed that successfully separated a suspension of SWCNTs dispersed in the CMC solution into four resulting samples: three different retentates and one permeate from the last step. The analysis of their optical absorption spectra showed that 75% of the starting SWCNTs were fractionated, leaving 25% probably on the filters and inner walls of the tubing as aggregates. AFM observations confirmed that the length distribution peaks in profiles of four separated samples are within the expected ranges from pore sizes of used filters. Additionally, it was found that both the permeation and reaggregation properties of dispersed SWCNTs in the filtration process greatly depend on their complex structure with detergent molecules.

EXPERIMENTAL SECTION

SWCNTs used in this study were synthesized by an enhanced direct-injection pyrolytic synthesis (eDIPS) method.²⁸ The purity of SWCNTs was >94 atom %, with a small amount of Fe nanoparticles remaining as impurities. As observed from a resonance Raman spectra of 514.5 nm laser excitation, the diameters of SWCNTs ranged from 1.38 to 1.68 nm,²⁴ and the G/D ratio was >173 . The typical Raman spectrum, as well as electron microscopy pictures of used SWCNTs, is shown in Supporting Information. A total of 4 mg of SWCNTs was dispersed in 200 mL of aqueous solutions of 1% CMC (MP Biomedicals low viscosity) or SDBS (Wako, purity $> 98.5\%$) with the help of bath sonication, and these suspensions were loaded in the cross-flow filtration system as source suspensions. The typical cross-flow filtration system used in the present study is a handmade apparatus converted from the commercially available filtration system, VIVAFLOW 50 (Sartorius Stedim Biotech), with an effective filtration area of 50 cm^2 , which was directly connected to a peristaltic pump by Tygon tubing, as shown in Figure 1a. We have adopted a hydrophilic polytetrafluoroethylene (PTFE) membrane (Millipore Omnipore) as filters in this system.

The filtration in each step was continued with the constant flow rate of 1 mL/s until the source suspension stopped decreasing. We have estimated that the reason for stopping the filtration is not the pressure induced by clogging of SWCNTs on the filter membrane, but the osmotic pressure induced by the increasing concentration of dispersants. It should be noted that this system is not a fully open system, but a semiclosed system like an ordinary dialysis system. Therefore the osmotic pressure is one of the most important factors to consider in the mechanism of filtration. To support this explanation, we have also carried out the following additional experiment. The retentate was diluted with a considerable amount of 1% aq CMC and again filtered with a new membrane. The resulting permeate was a colorless clear solution, and the volume was almost the same as the added amount of aq. CMC solution. Of course the volume of the reobtained retentate was almost the same as that of the initial one. In the case of using SDBS as a detergent or CMC suspension without SWCNTs, source suspensions permeated through all filters completely.

Separated samples A–D were characterized by optical absorption spectroscopy (Hitachi, U-4100) and atomic force micros-

copy (AFM) observations (SII NanoTechnology Inc., SPA400). To investigate the filtration efficiency, relative amounts of SWCNTs in these samples were calculated from the average of photo absorption in the whole measured range, which has been discussed in the Results and Discussion.

Specimens for AFM measurements were prepared by following procedures. Silicon (Si) substrates were chemically functionalized by using aminopropyltrimethoxysilane (APTES). SWCNT suspensions were dropped on the functionalized Si substrates and washed with water to remove detergent. This procedure was repeated until the frequency of SWCNTs in the AFM image became suitable for the investigation of their length distribution. Lengths of more than 300 SWCNTs were measured in each samples for the statistical operation.

Supporting Information Available: SEM and TEM images (Figure S1) and the typical resonance Raman spectrum (Figure S2) of used SWCNTs in the present work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Acknowledgment. This work is partially supported by the New Energy and Industrial Technology Development Organization (NEDO).

REFERENCES AND NOTES

1. Cao, Q.; Rogers, J. A. Random networks and aligned arrays of single-walled carbon nanotubes for electronic device applications. *Nano Res.* **2008**, *1*, 259–272.
2. Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Elsevier: San Diego, 1996.
3. Dai, H. Carbon nanotubes: Synthesis, integration, and properties. *Acc. Chem. Res.* **2002**, *35*, 1035–1044.
4. Tanaka, K.; Okahara, K.; Okada, M.; Yamabe, Y. Electronic properties of bucky-tube model. *Chem. Phys. Lett.* **1992**, *191*, 469–472.
5. Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. Electronic structure of graphene tubules based on C_{60} . *Phys. Rev. B* **1992**, *46*, 1804–1811.
6. Hamada, N.; Sawada, S.; Oshiyama, A. New one-dimensional conductors: Graphitic microtubules. *Phys. Rev. Lett.* **1992**, *68*, 1579–1581.

- Fagan, J. A.; Simpson, J. R.; Bauer, B. J.; De Paoli Lacerda, S. H.; Becker, M. L.; Chun, J.; Migler, K. B.; Hight Walker, A. R.; Hobbie, E. K. Length-dependent optical effects in single-wall carbon nanotubes. *J. Am. Chem. Soc.* **2007**, *129*, 10607–10612.
- Rajan, A.; Strano, M. S.; Heller, D. A.; Hertel, T.; Schulten, K. Length-dependent optical effects in single walled carbon nanotubes. *J. Phys. Chem. B* **2008**, *112*, 6211–6213.
- Sun, X.; Zaric, S.; Daranciang, D.; Welsher, K.; Lu, Y.; Li, X.; Dai, H. Optical properties of ultrashort semiconducting single-walled carbon nanotube capsules down to sub-10 nm. *J. Am. Chem. Soc.* **2008**, *130*, 6551–6555.
- Pike, G. E.; Seager, C. H. Percolation and conductivity: A computer study. I*. *Phys. Rev. B* **1974**, *10*, 1421–1434.
- Hu, L.; Hecht, D. S.; Grüner, G. Percolation in transparent and conducting carbon nanotube networks. *Nano Lett.* **2004**, *4*, 2513–2517.
- Simien, D.; Fagan, J. A.; Luo, W.; Douglas, J. F.; Migler, K.; Obrzut, J. Influence of nanotube length on the optical and conductivity properties of thin single-wall carbon nanotube networks. *ACS Nano* **2008**, *2*, 1879–1884.
- Ziegler, K. J.; Schmidt, D. J.; Rauwald, U.; Shah, K. N.; Flor, E. L.; Hauge, R. H.; Smalley, R. E. Length-dependent extraction of single-walled carbon nanotubes. *Nano Lett.* **2005**, *5*, 2355–2359.
- Duesberg, G. S.; Muster, J.; Krstic, V.; Burghard, M.; Roth, S. Chromatographic size separation of single-wall carbon nanotubes. *Appl. Phys. A: Mater. Sci. Process.* **1998**, *67*, 117–119.
- Zheng, M.; Jagota, A.; Semke, E. D.; Diner, B. A.; Robert, S.; Mclean, R. S.; Lustig, S. R.; Richardson, R. E.; Tassi, N. G. DNA-assisted dispersion and separation of carbon nanotubes. *Nat. Mater.* **2003**, *2*, 338–342.
- Huang, X.; Mclean, R. S.; Zheng, M. High-resolution length sorting and purification of DNA-wrapped carbon nanotubes by size-exclusion chromatography. *Anal. Chem.* **2005**, *77*, 6225–6228.
- Fagan, J. A.; Becker, M. L.; Chun, J.; Nie, P.; Bauer, B. J.; Simpson, J. R.; Hight-Walker, A.; Hobbie, E. K. Centrifugal length separation of carbon nanotubes. *Langmuir* **2008**, *24*, 13880–13889.
- Fagan, J. A.; Becker, M. L.; Chun, J.; Hobbie, E. K. Length fractionation of carbon nanotubes using centrifugation. *Adv. Mater.* **2008**, *20*, 1609–1613.
- Doorn, S. K.; Fields, R. E.; Hu, H.; Hamon, M. A.; Haddon, R. C.; Selegue, J. P.; Majidi, V. High resolution capillary electrophoresis of carbon nanotubes. *J. Am. Chem. Soc.* **2002**, *124*, 3169–3174.
- Daniel, A.; Heller, D. A.; Mayrhofer, R. M.; Baik, S.; Grinkova, Y. V.; Usrey, M. L.; Strano, M. S. Concomitant length and diameter separation of single-walled carbon nanotubes. *J. Am. Chem. Soc.* **2004**, *126*, 14567–14573.
- Chen, B.; Selegue, J. P. Separation and characterization of single-walled and multiwalled carbon nanotubes by using flow field-flow fractionation. *Anal. Chem.* **2002**, *74*, 4774–4780.
- Chun, J.; Fagan, J. A.; Hobbie, E. K.; Bauer, B. J. Size separation of single-wall carbon nanotubes by flow-field flow fractionation. *Anal. Chem.* **2008**, *80*, 2514–2523.
- Saito, T.; Ohmori, S.; Shukla, B.; Yumura, M.; Iijima, S. A novel method for characterizing the diameter of single-wall carbon nanotubes by optical absorption spectra. *Appl. Phys. Exp.* **2009**, *2*, 095006.
- Jorio, A.; Saito, R.; Hafner, J. H.; Lieber, C. M.; Hunter, M.; McClure, T.; Dresselhaus, G.; Dresselhaus, M. S. Structural (*n,m*) determination of isolated single-wall carbon nanotubes by resonant Raman scattering. *Phys. Rev. Lett.* **2001**, *86*, 1118–1121.
- O'Connell, M.; Bachilo, S. M.; Huffman, C. B.; Moore, V.; Strano, M. S.; Haroz, E.; Rialon, K.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J.; Hauge, R. H.; Weisman, R. B.; Smalley, R. E. Band gap fluorescence from individual single-walled carbon nanotubes. *Science* **2002**, *297*, 593–596.
- Richard, C.; Balavoine, F.; Schultz, P.; Ebbesen, T. W.; Mioskowski, C. Supramolecular self-assembly of lipid derivatives on carbon nanotubes. *Science* **2003**, *300*, 775–778.
- Abatemarco, T.; Stickel, J.; Belfort, J.; FrankB, P.; Ajayan, P. M.; Belfort, G. Fractionation of multiwalled carbon nanotubes by cascade membrane microfiltration. *J. Phys. Chem. B* **1999**, *103*, 3534–3538.
- Saito, T.; Ohshima, S.; Okazaki, T.; Ohmori, S.; Yumura, M.; Iijima, S. Selective diameter control of single-walled carbon nanotubes in the gas-phase synthesis. *J Nanosci. Nanotechnol.* **2008**, *8*, 6153–6157.