Probing the mechanics of aqueous two-phase extraction using large diameter single-walled carbon nanotubes

Edyta Turek[a], Tomasz Wasiak[a], Grzegorz Stando[a], Dawid Janas[a,*]

a Department of Chemistry, Silesian University of Technology, B. Krzywoustego 4, 44-100 Gliwice, Poland

Abstract

We have demonstrated that large diameter (1.8±0.4 nm) carbon nanotubes (CNTs) can be separated by means of the aqueous two phase extraction (ATPE). This rapid and convenient tool has enabled us to isolate fractions of particular CNT diameter distribution. We have shown how a range of parameters can be used to fine tune the characteristics of the isolated material. What is very interesting, by varying the pH of the medium, we have suppressed the extraction of low diameter CNTs and only large diameter CNTs were obtained. A number of other factors such as selected surfactant concentration steps, temperature or amount of starting CNT material have been found to have a significant effect on the end result of the CNT differentiation. The findings have provided us with more insight regarding the underlying mechanics of ATPE for processing polydisperse CNT mixtures.

Introduction

Despite being made just of carbon atoms, single-walled carbon nanotubes (SWCNTs) show a great deal of structural complexity. This seemingly seamless cylinders made from graphene hexagonal lattice can be arranged in a wide range of ways. The particular arrangement of carbon atoms in a tube can be quantified by the so-called chiral angle (n,m) often referred to as chirality in this context. The chirality has got a dramatic effect on electrical [1, 2], optical [3-5], thermal [6, 7] and other properties of the individual SWCNTs. To pin-point the role of

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* Corresponding author. Tel/Fax: +48 32 2372958. E-mail address: dawid.janas@polsl.pl (D. Janas).

this parameter and also bring the material much closer to implementation, the community has focused the efforts on devising an arsenal of SWCNT sorting techniques [8, 9].

At present, there are four main stream methods used to reach this goal: ultracentrifugation in density gradient [10], chromatography [11, 12], selective-dispersion with particular polymers [13, 14] and the aqueous two-phase extraction (ATPE) [15]. The latter approach is particularly attractive as it is quick, straightforward and does not involve expensive apparatus [15-17]. Unfortunately despite its merits, the results published so far are mostly based on HiPco SWCNTs, which are much easier to sort because of their small diameter (d ≈ 1 nm). In a recent contribution by Fagan *et al.* [18], the authors demonstrated ATPE sorting capabilities with SWCNTs up to 1.7 nm in diameter. We wanted to go a step further and made a thorough analysis how different parameters affect differentiation of SWCNTs with 1.8±0.4 nm diameter distribution. Large diameter SWCNTs of defined structure are highly promising for the semiconductor industry [19]. Reduced Schottky barrier [20] and high saturation current [21] can be key for the SWCNTs to replace traditionally used materials in microelectronics one day. Moreover, large diameter SWCNTs are very appealing for the photonic applications as they emit light in the telecommunication range and can be employed for quantum information processing [22, 23]. To this day, SWCNTs as large as 10 nm diameters were reported, but they still await appropriate applications to fully utilize their properties [24].

In this contribution, we present our results of sorting large diameter SWCNTs by using the ATPE method. By varying the amount of CNTs, surfactants, concentration steps, temperature, pH and adding kosmotropic salt we probed the underlying mechanics of separation. The results showed the most optimal parameters to obtain SWCNTs of particular diameter distribution. Analysis of phase composition from all the separation steps enabled us to draw conclusions regarding the course of separation. We demonstrate how the multi-parameter space of aqueous two-phase system can be tuned with high sensitivity.

1. Experimental

SWCNTs of high purity were procured from OCSiAl (Tuball[TM]) and purified by air treatment and reflux in HCl according to a published routine [25]. All other chemicals (Dextran (PEG) M_w=70,000 g/mol, PEG M_w=6,000 g/mol, sodium dodecyl sulphate (SDS), sodium deoxycholate (DOC), hydrochloric acid, sodium hydroxide and ammonium phosphate) were of analytical grade (Avantor).

SWCNTs (1 mg/mL) were dispersed in water using 20 g/L of DOC. The mixture was homogenized by a tip sonicator for 2 hours (Hielscher UP50H). Next, the dispersion was centrifuged at 11,000 rpm (Eppendorf 5804R) for 2 h to remove the non-individualized SWCNTs from the dispersion (top 80% of the supernatant was used for the study).

ATPE was carried out by modifying an approach published by Fagan *et al.* [18] Two pre-concentration steps were employed to reduce the amount of used compounds. First, 4 parts of SWCNT dispersion were combined with 4 parts of DEX (20%, aq.) and 2 parts of PEG (25%, aq.). Then, the mixture was centrifuged (2000 rpm, 3 min) to separate into two phases. The grey bottom phase was taken to the following step, wherein it was combined with 3 parts each of DEX (7.2%, aq.), PEG (10%, aq.) and SDS (0.6%, aq.). Again the SWCNTs separated into the bottom phase. Stepwise addition of top phase mimic enabled separation. The conditions of each experiment are given in the Supplementary Information file.
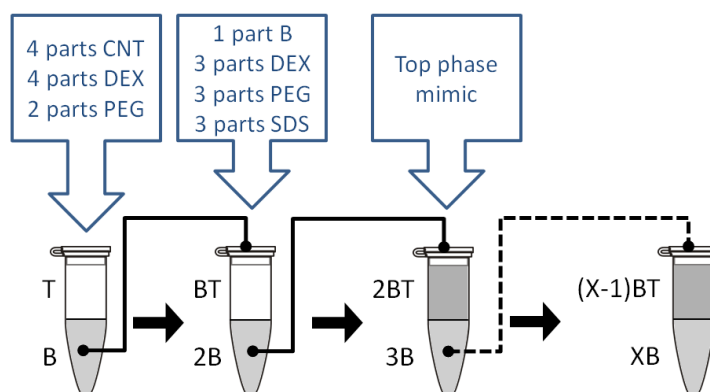

Fig. 1 The method of separation used in the study – ATPE.

Temperature was controlled by keeping the samples in a bath, wherein addition of appropriate aqueous phases took place.

Calculated amounts of hydrogen chloride or sodium hydroxide were used to adjust the pH of the ATPE mixture. The values were verified by a digital pH meter before the phases separated.

Ammonium phosphate (aq.) was used as the model kosmotropic salt to influence the course of ATPE.

Absorbance spectra were obtained from 400 to 1000 nm using Hitachi U-2910 spectroscope. Absorption spectroscopy enables high-throughput characterization of SWCNT diameter as compared with TEM or AFM [26].

Scanning Electron Microscopy (SEM, FEI Nova NanoSEM) was employed to analyse the microstructure of the material.

Raman spectroscopy (inVia Renishaw Raman microscope, λ=633 nm) was used to record inelastic scattering from the samples within 50 to 3200 cm^{-1} range. To lower the effect of background and improve the obtained spectra, 50 accumulations were acquired for each sample.

2. Results and discussion

2.1. Characterization of the material

It is very important to use SWCNTs, which are essentially free of functionalization for differentiation. The presence of functional groups would not only interfere with the sorting outcomes, but it would make the results much less reproducible. We used Raman spectroscopy (Fig. 1a,b) and SEM to verify the suitability of the selected material.
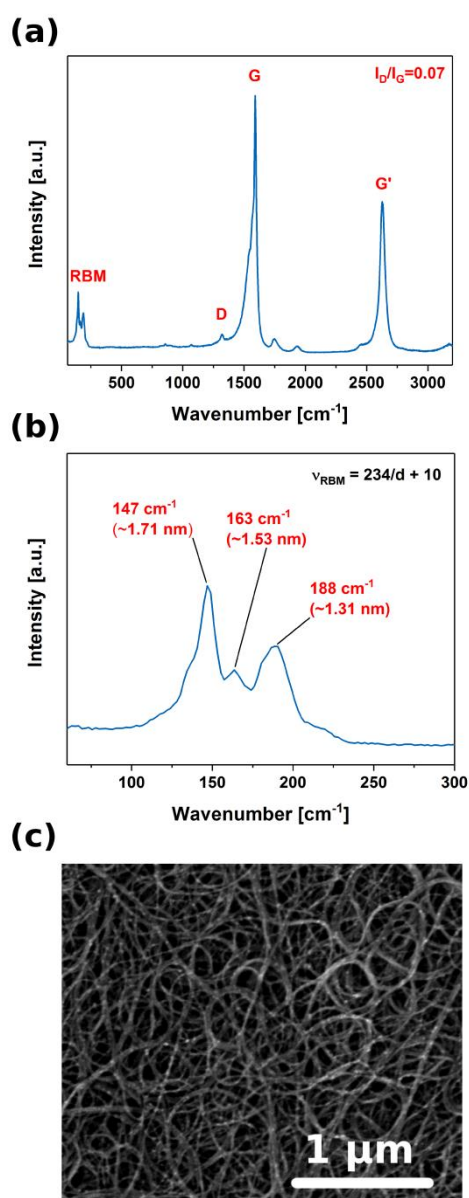

Fig. 2 Characterization of the parent material. (a) Raman spectra with close-up plot of (b) RBM area. (c) SEM micrograph.

The SWCNTs were of very high purity as gauged by the I_D/I_G ratio of just 0.07 (Fig. 1a) or XPS analysis carried out by us previously [27]. Another indirect proof of highly defined structure is slight splitting of the G band into G- and G+ [28]. Moreover, the peaks in the RBM area (Fig. 1b) were clearly noticeable. By using the relation of their wavenumber to diameter [29, 30], we were able to estimate the diameter of the excited SWCNTs to be 1.71 nm, 1.53 nm and 1.31 nm by 633 nm laser. The obtained values fall within the outer mean diameter range provided by the manufacturer (1.8±0.4 nm). Due to the resonant nature of this technique we could not observe SWCNTs with larger diameter than 1.71 nm. From the microstructure point of view, SEM confirmed that the SWCNTs are of high purity (Fig. 1c). Carbonaceous deposits, which are a common by-product of the synthesis, could not be discerned. Due to the high bundling degree we decided to sonicate the material for a prolonged amount of time (2 hours) to individualized SWCNTs to appropriate extent.

2.2. Surfactant effect

We wanted to find out, which of two surfactants (increasing concentration of SDS or decreasing concentration of DOC) enables better control over the course of ATPE (Fig. 3).
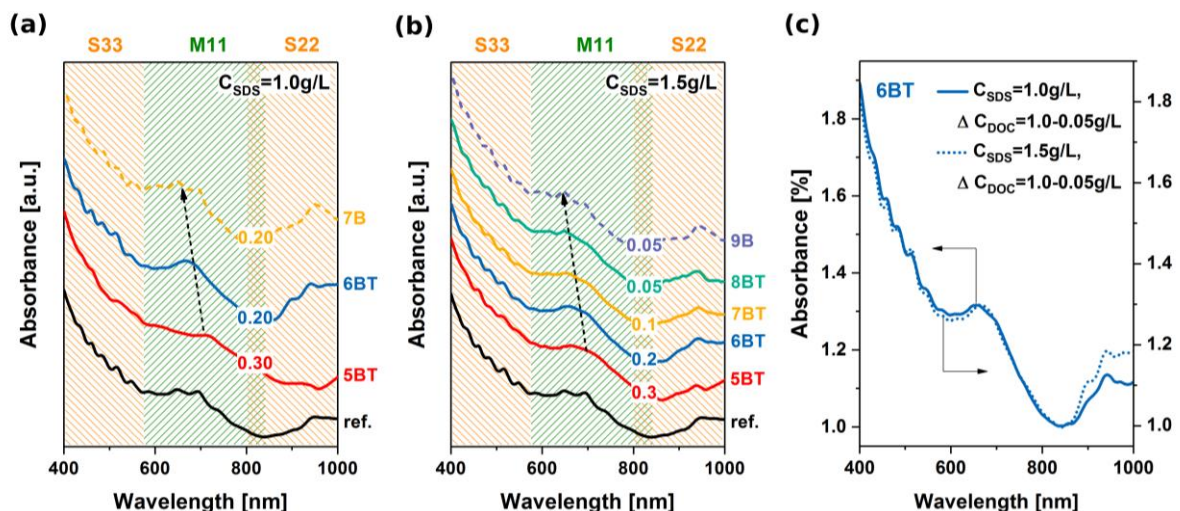

Fig. 3 ATPE controlled by addition of decreasing concentrations of DOC at constant SDS concentration of (a) 1.0 g/L, (b) 1.5 g/L. Comparison of spectra from 6BT phases having the same DOC concentration, but different content of SDS.

Fagan *et al.* reported that one can differentiate the SWCNTs by stepwise decrease in DOC concentration with each mimic phase [16]. The starting material that they used was of predominantly (6,5) chirality, and hence they could not study in details how addition of DOC of different concentration affects the separation of SWCNT mixture composed of a wide range of chiralities. According to our results, with decreasing DOC concentration from 1.0 g/L to 0.20 g/L (1.0, 0.75 and 0.50 g/L not shown) smaller diameter SWCNTs are separated (Fig. 3a). It can be noticed that the conditions of this ATPE (C_{SDS}=1.0 g/L) were not optimized: the SWCNTs appeared only as late as 5BT, 6BT and 7B fractions. At this point, a predominant amount of material was lost at the interface (one of the drawbacks of ATPE method [31]) and further separation was not possible. To increase the resolution, we decided to increase the starting SDS concentration from 1.0 to 1.5 g/L (Fig. 3b). Much less material was lost at the interface, which made it possible to carry out two more separation steps eventually reaching C_{DOC}=0.05 g/L (using the same DOC concentration steps). In this case, the diameter of the selected nanotubes also decreased with decreasing concentration of introduced DOC. Again, no SWCNTs were isolated at 1.0, 0.75 and 0.50 g/L DOC concentration despite higher SDS content. Furthermore, comparison of 6BT spectra from both separation rounds indicated that the same diameter profile of SWCNTs is isolated regardless of the starting concentration of SDS (Fig. 3c). However, increased concentration of SDS helped to improve the yield of the separation as indicated by higher intensity of the peaks in S22 range (dotted line). The finding was in accordance with the lower concentration of SWCNTs present at the interface postulated before.

Because some of the material is lost at the interface each time the separation is executed, the number of necessary steps to obtain a particular type of SWCNTs should be limited (or the starting dispersion volume increased). To tackle this problem we focused on the optimization

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of the concentrations steps of used SDS (Fig. 4). For the first attempt, we selected a range of concentrations up to 1.5 g/L (0.15, 0.25, 0.50, 0.75, 1.00 and 1.50 g/L, Fig. 4a).
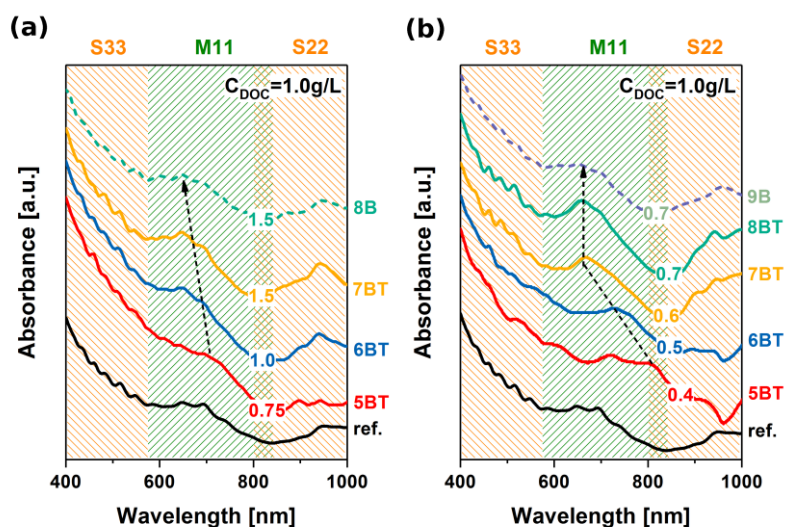

Fig. 4 ATPE controlled by addition of increasing concentrations of SDS at constant DOC concentration. (a) large and (b) small SDS concentration step (shown in g/L).

The SWCNTs were first detected at 0.75 g/L SDS in 5BT phase. Further increase in SDS concentration up to 1.5 g/L resulted in separation of gradually lower diameter SWCNTs. In the next step, we made an attempt to decrease the SDS concentration step (Fig. 4b). Lower diameter SWCNTs were gradually isolated up to 0.6 g/L SDS, but then no further decrease of SWCNT diameter could be observed. The final shape of the 9B curve in Fig. 4c (0.7 g/L SDS) very much resembles the 8B curve from Fig. 4a (1.5 g/L SDS). The results strongly suggest that running the ATPE by modifying the SDS concentration the separation has got a "*vectorial*" character. The most important is the separation course and what SWCNTs are isolated at each stage rather than the used absolute surfactant concentrations. Interestingly, we found out that certain separation steps can be skipped without affecting the ATPE only when no SWCNTs migrate into between phases (Fig. 5). We noticed that, under regular ATPE conditions, at 0.1 and 0.2 g/L SDS no SWCNTs can be found in the top phases.

Skipping these steps and going directly to 0.3 g/L SDS (Fig. 5b) did not make any significant difference to the separation course (Fig. 5c). The absorption curves from 6BT phases appear almost exactly the same as the one from the complete ATPE protocol.
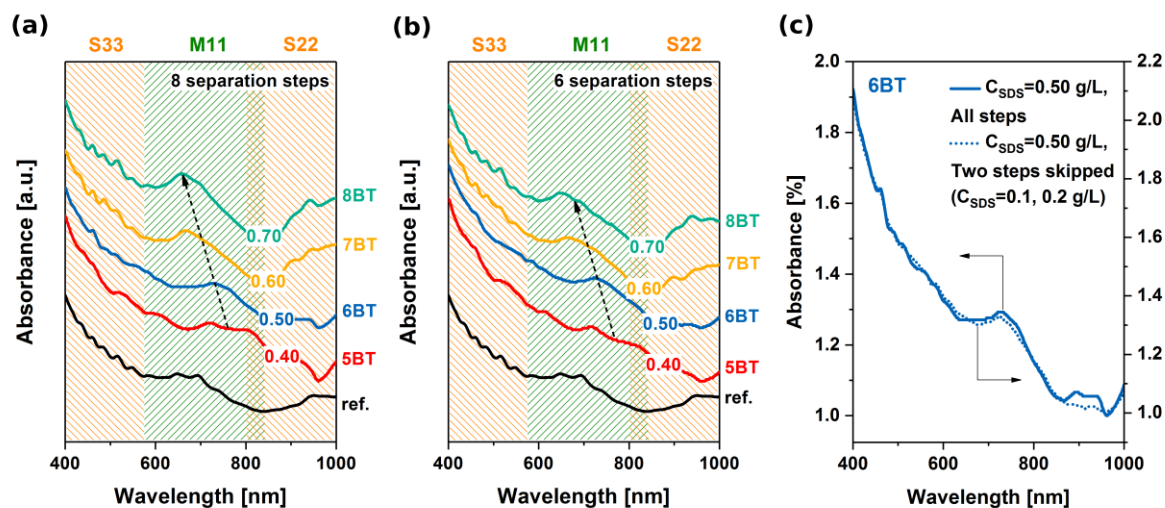

Fig. 5 ATPE carried out (a) with all the intermediate concentrations, (b) without 0.1% and 0.2% SDS (aq.) concentrations. (c) Comparison of spectra from 6BT phases having different number of separation steps. Increasing SDS concentration in g/L is shown in the plots.

From the results presented so far it is clear that the DOC or SDS concentration is very important as it causes distribution of SWCNTs between the two phases. It was reported that the bottom DEX phase is relatively more hydrophilic that PEG, which is considered more hydrophobic [15]. In light of this report and our findings, increase in DOC concentration seems to push the SWCNTs into the hydrophilic bottom phase whereas increase in SDS concentration shifts them to the hydrophobic top phase. Either DOC has got a more hydrophilic character than SDS or these two surfactants show a particular preference towards PEG and DEX aqueous dispersions, respectively. Regardless of the surfactant used, first the large diameter SWCNTs are isolated, which is followed by the ones of smaller diameter.

2.3. Temperature effect

Higher temperature enables better mobility of the SWCNTs between the two phases due to thermal motion, which in turn increases the resolution and the yield of the separation (Fig. 6). By increasing the temperature from 20°C (Fig. 6a) to 30°C (Fig. 6b) we were able to register the presence of SWCNTs in the top phases sooner (4BT 0.50 g/L *vs.* 5 BT 0.75 g/L SDS).
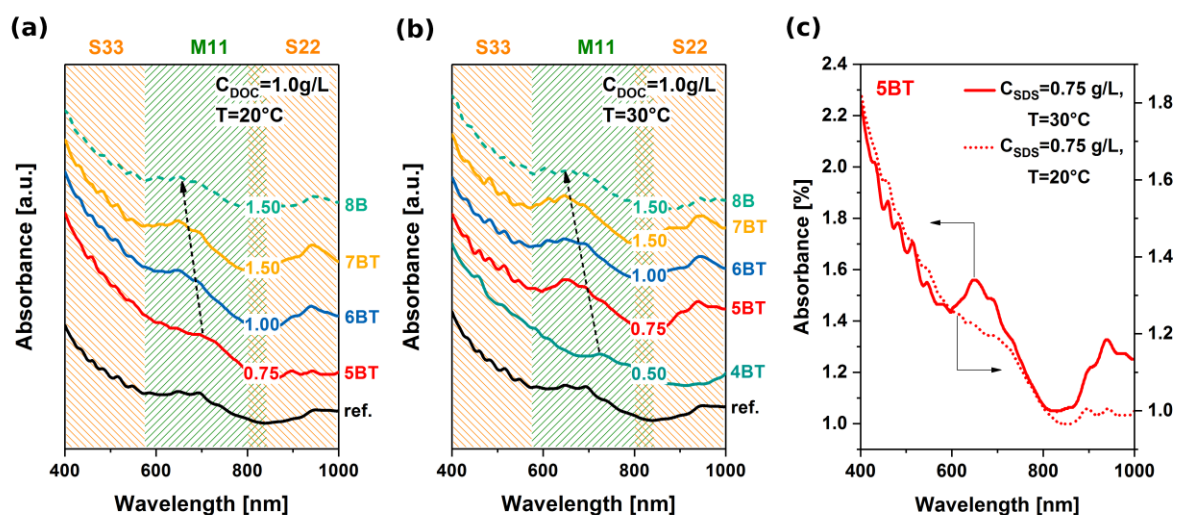

Fig. 6 ATPE carried out at (a) 20°C, (b) 30°C. (c) Comparison of spectra from 5BT phases obtained at different temperatures. Increasing SDS concentration in % is shown in the plots.

As a consequence, higher temperature separations under the same chemical environment give rise to separation of slightly smaller diameter SWCNTs (Fig. 6c). The yield is also improved as less material is lost at the interface as indicated by stronger and more defined peaks in the spectra of corresponding diameter distributions (e.g. Fig. 6a 6BT *vs.* Fig. 6b 5BT). Further increase in temperature up to 40°C (not shown) did not cause a notable increase in ATPE performance. High temperature can cause surfactant desorption from the surface of SWCNTs, so one has to be careful when tuning the separation using this parameter.

2.4. Salt effect

Addition of salts into the ATPE system may have a strong effect on the distribution of SWCNTs between the two phases. It has been reported that NaSCN (chaotropic salt) pushes SWCNTs into the bottom phase [15], whereas NaCl (kosmotropic salt) has got an opposite effect [31]. Since kosmotropic ammonium phosphate was found to be effective in molecular biology (significantly increased the yield of chromatographic separation of antibodies [32]), we wanted to evaluate it herein for separation purposes as well.
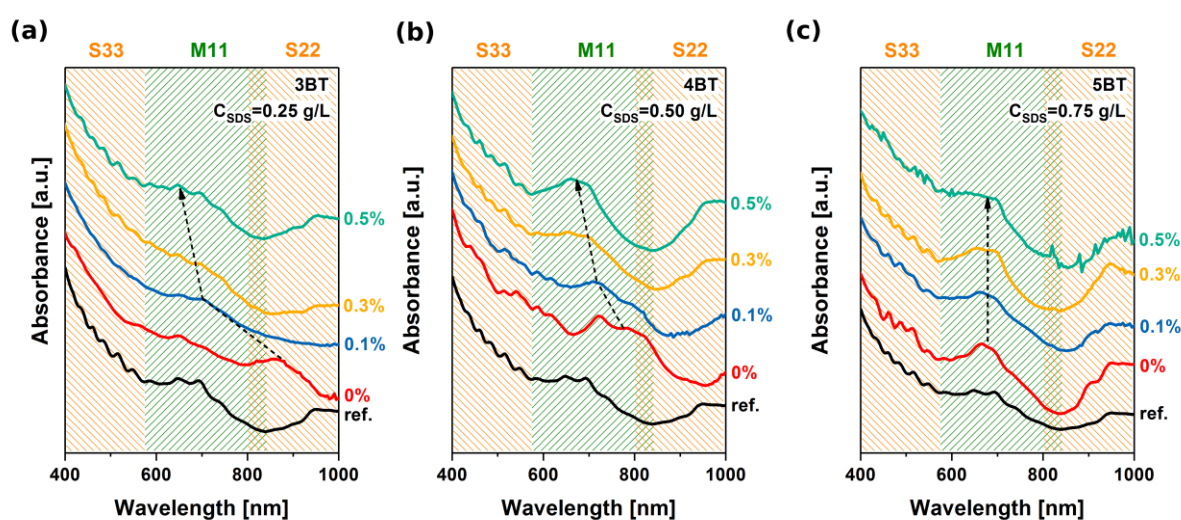

Fig. 7 (a) 3BT, (b) 4BT and (c) 5BT phases of different content of kosmpotropic salt.

Addition of ammonium phosphate indeed moves more of small diameter SWCNTs into the top phase. What is interesting, the effect is the most powerful in the initial separation steps (see the slope of the arrows). Addition of just 0.1% of ammonium phosphate into the step leading to the 3BT phase significantly shifted the SWCNT diameter distribution towards lower values. Moreover, higher salt content (0.3% or 0.5%) also causes extraction of more of small diameter SWCNTs by the 3BT PEG phase, but not to the same extent. In the next separation step we also observed the same trend, but the effect for the 0.1% 4BT phase was slightly less prominent although still the strongest among the tested samples. In the final step, we do not see any differences between all the 5BT samples regardless of the amount of salt.

The reason for that is under these conditions all the remaining SWCNTs shifted into the top phase and there are no more of SWCNTs of the larger diameter in the bottom phase to extract.

2.5.Starting SWCNT volume effect

Since the relative content of a particular surfactant was found to influence the results of ATPE, we wanted to evaluate how change in the amount of injected SWCNT dispersion affected the separation (Fig. 8).
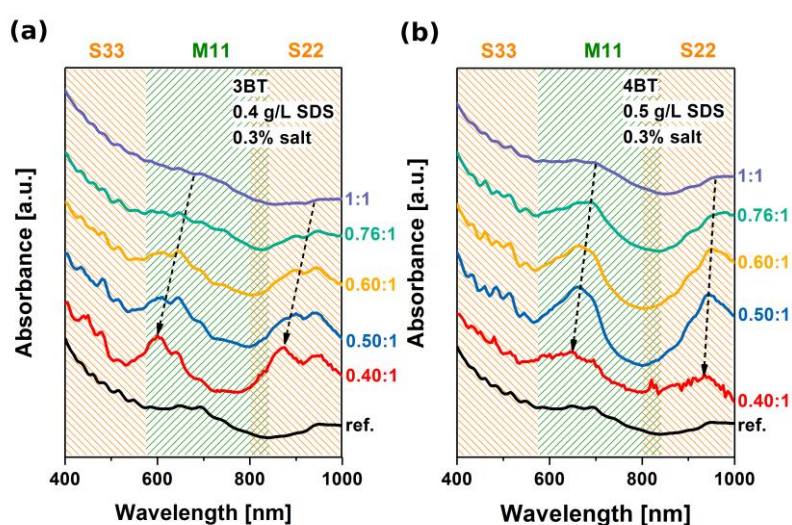

Fig. 8 (a) 3BT and (b) 4BT phases of ATPE carried out in the presence of 0.3% kosmpotropic salt using different ratio of starting parent SWCNT dispersion to all the other components of ATPE system.

For this experiment we also employed 0.3% of ammonium phosphate to facilitate the migration of SWCNTs to the top phase. Lowering the amount of introduced SWCNTs had a strong effect on the diameter distribution of separated SWCNTs – gradually lower diameter SWCNTs were shifted to the top phase. In such arrangement, there was more polymer species per SWCNT to cause their transfer to PEG layer. Furthermore, the peaks in the absorption curves became sharper. Samples from 0.60:1 or 0.50:1 ratio in the 4BT phase were

particularly defined with a clear minimum between M11 and S22 range. One has to be careful not to sacrifice the resolution as the ATPE is *"sped up"* by lowering the amount of employed SWCNTs. Separation carried out using 0.40:1 is an example of such case, wherein the signal from SWCNTs faded already at 4BT phase (Fig. 8b).

2.6. pH effect

pH was found to have a strong influence on the course of SWCNT separation when chromatography was selected as the separation method [19, 33].
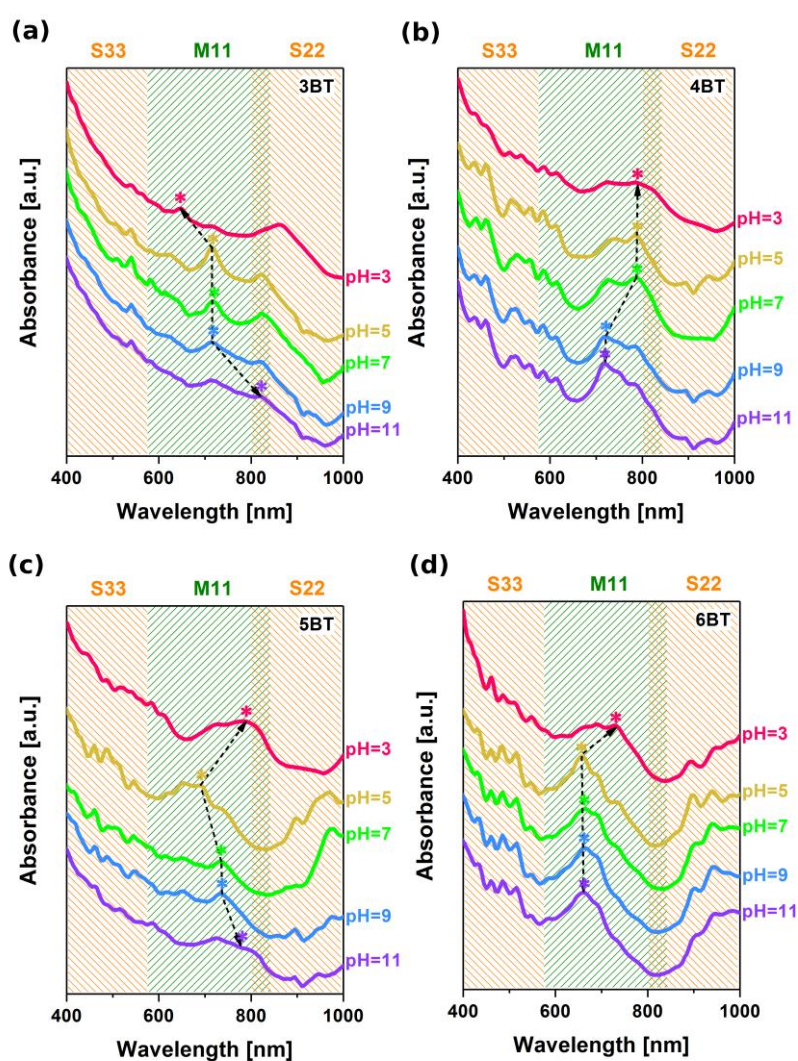

Fig. 9 (a) 3BT, (b) 4BT, (c) 5BT and (d) 6BT phases of ATPE carried out at different pH conditions. Peaks with highest intensity in the M11 region were indicated with an asterisk.

In our case, we observed that, when ATPE was used as a differentiation method, pH had non-monotonic influence on the diameter distribution of obtained SWCNTs at every stage (Fig. 9). It is clear that at pH 3 the separation gives only the biggest diameter SWCNTs (peaks are shifted towards longer absorption wavelengths). The presence of a protonating agent was found to have a strong effect on the shape of the SWCNT micelles [33], which is crucial for extraction. By using low pH conditions we supressed the migration of small diameter SWCNTs to the top phase and they remained in the bottom phase or at the interface. Nevertheless, stepwise differentiation among those large diameter SWCNTs was possible from 3BT to 6BT. Increasing the pH to 5 clearly affects the diameter distribution. The maximum peak intensity throughout the whole spectra is always less or equal the corresponding one recorded at pH 3. That indicates that with increase of pH in this range smaller or equal diameter SWCNTs are obtained. Further increase of pH from 5 to 7 does not result in evident changes with the exception of 5BT phase, wherein larger diameter SWCNTs are the dominant fraction. Interestingly, carrying out ATPE in basic conditions has the opposite effect on diameter distribution (3BT, 4BT) as compared with separation in acidic conditions. Yang and co-workers described that redox reactions have a peculiar preference towards SWCNTs diameter [19]. Reduction processes (in the presence of OH-) preferentially occur on small diameter SWCNTs with large bandgaps in contrast with oxidation processes (in the presence of H+), which affect large diameter SWCNTs with small bandgaps in the first instance. A very good demonstration how this influences the separation was given by Gui *et al.*, who carried out one-step ATPE in the presence of NaClO or $NaBH_4$ as oxidant and reductant agent, respectively [17]. When the separation was done in semi-reduced or semi-oxidized conditions, the phase composition was exactly reversed – what was the top phase under one condition, was the bottom under the other condition and conversely. Further increase in oxidant or reductant content beyond a certain threshold resulted in migration of all

of the SWCNTs to the bottom phase. In our case, phases 3BT and 4BT, wherein we used pH change instead of adding these agents, mimic this behaviour closely. However, phase 5BT resembles the results from fully-reduced and fully-oxidizing extractions from the referred work. The maximum peak intensity of pH 3 and pH 11 phases is very similar with an upturn point of this trend at pH 5. Finally, the 6BT phases (pH 5, 7, 9, 11) have a very similar content (smallest diameter SWCNTs were isolated) in contrast with the 6BT phase from pH 3 as described before (suppression of extraction of smallest diameter SWCNTs under these conditions). Unfortunately separation at pH 1 was not possible as surfactants desorbed from SWCNTs causing their agglomeration.

3. Conclusions

We presented a range of parameters, which can influence the results of the differentiation of large diameter SWCNTs by the ATPE method. SDS and DOC had an opposite effect and with increasing/decreasing content, smaller diameter SWCNTs were separated, respectively. Alternatively, the relative amount of SWCNTs to be separated can be varied. One has to keep in mind that the number of steps of ATPE separation is limited because always some material is lost at the interface. As a consequence, it is very important to adjust the concentration step of the added surfactant to extract the desired types of the SWCNTs. As we found out, separation steps, at which no SWCNTs migrate between phases can be skipped and have no influence on the course of separation. Moreover, slight increase in temperature from 20°C to 30°C improved the separation yield as less material was lost at the interface. Unfortunately further increase in temperature up to 40°C did not result in any more separation enhancement. Next, addition of ammonium phosphate proved to be an effective way to enrich the top phase with lower diameter SWCNTs. Care has to be taken however as this effect was found to decrease the resolution of separation under certain circumstances. Changing the pH had the most complex influence on the resulting SWCNT diameter distribution, which were

extracted. The most interesting conditions were those at pH 3 wherein we supressed migration of small diameter SWCNTs and only the large diameter SWCNTs were obtained.

The results show that ATPE separation is also valid for larger diameter SWCNTs despite the fact that with increasing diameter the minute structural differences between the neighbouring chiralities, which give rise to differentiation, become less evident. The methodology presented herein can be a very good base for isolation of SWCNTs of particular large diameter distribution for microelectronics or photonics when purity at the level of single chirality is not necessary.

4. Competing financial interests

The authors declare that there is not any competing financial interest in relation to the work described.

5. Acknowledgements

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