SILESIAN UNIVERSITY OF TECHNOLOGY
FACULTY OF CHEMISTRY
DEPARTMENT OF ORGANIC CHEMISTRY, BIOORGANIC CHEMISTRY AND BIOTECHNOLOGY

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DOCTORAL DISSERTATION

Extended summary

Rozdział mieszanin nanorurek węglowych metodą dwufazowej ekstrakcji wodnej

Separation of carbon nanotube mixtures by aqueous two-phase extraction method

Promoter: dr hab. inż. Dawid Janas, prof. PŚ

Gliwice 2023

List of the main publications resulting from the thesis

[P1] Podlesny, B.; Shiraki, T.; Janas, D. One-Step Sorting of Single-Walled Carbon Nanotubes Using Aqueous Two-Phase Extraction in the Presence of Basic Salts. Sci. Rep. 2020, 10 (1), 9250. https://doi.org/10.1038/s41598-020-66264-7.
(IF_{2020} = 4.380, MEiN = 140 points)

[P2] Podlesny, B.; Kumanek, B.; Borah, A.; Yamaguchi, R.; Shiraki, T.; Fujigaya, T.; Janas, D. Thermoelectric Properties of Thin Films from Sorted Single-Walled Carbon Nanotubes. Materials (Basel). 2020, 13 (17), 3808. https://doi.org/10.3390/ma13173808.
(IF_{2020} = 3.623, MEiN = 140 points)

[P3] Podlesny, B.; Olszewska, B.; Yaari, Z.; Jena, P. V.; Ghahramani, G.; Feiner, R.; Heller, D. A.; Janas, D. En Route to Single-Step, Two-Phase Purification of Carbon Nanotubes Facilitated by High-Throughput Spectroscopy. Sci. Rep. 2021, 11 (1), 10618. https://doi.org/10.1038/s41598-021-89839-4.

(IF_{2021} = 4.997, MEiN = 140 points)

[P4] Podlesny, B.; Hinkle, K.R.; Hayashi, K.; Niidome, Y.; Shiraki, T.; Janas, D., Highly-Selective Harvesting of (6,4) SWCNTs Using the Aqueous Two-Phase Extraction Method and Non-Ionic Surfactants. Adv. Sci. 2023, in press, https://doi.org/10.1002/advs.202207218
(IF_{2021} = 17.521, MEiN = 200 points)

Cumulative IF = 30.521, Average IF = 7.630, Overall 620 MEiN points

Introduction

Due to their physical and chemical properties, single-walled carbon nanotubes (SWCNTs) have greatly interested the scientific community for several decades. The structure of SWCNTs resembles a simple cylinder created by rolling up a graphene sheet. Rolling up graphene is not the same for all nanotubes, so different species can be distinguished, differing in chirality indices (n, m), simply called "chirality"[1].

SWCNTs of dissimilar chiralities show different electrical[2], optical[3,4], thermical[5], and mechanical properties[6]. The current level of technological advancement does not yet offer effective synthesis methods of SWCNTs with precisely defined properties, so separation methods that enable efficient isolation of material with specific characteristics are highly wanted[7]. One of the commonly employed techniques to achieve chiral purity is aqueous two-phase extraction (ATPE).

ATPE is based on the preferential migration of analytes to one of two aqueous phases, formed by compounds of the appropriate concentration and significant differences in hydrophilicity[8]. Extraction systems usually consist of two polymers or polymer and salt[9]. One of the most popular combinations is the dextran (DEX)-poly(ethylene glycol) (PEG) system, which is successfully used to separate SWCNTs.

The classical separation of SWCNTs by the ATPE method includes the following steps:

- introduction of ATPE system components: phase-forming compounds, SWCNTs dispersion in aqueous surfactant solutions, surfactants solution, and modulators (when required). Generally, the process is conducted in centrifuge tubes.

- homogenisation of the sample

- centrifugation to facilitate formation of two phases

- collection of obtained phases and analysis or further processing

Surfactants are crucial for the separation of SWCNTs by the ATPE method. Selection of the appropriate one determines to which of the phases the introduced SWCNT dispersion spontaneously diffuses. To differentiate the material between the phases, a co-surfactant must be introduced, which will cause some part of the material to migrate to the opposite phase. Thus, SWCNT separation relies on competitive adsorption of surfactants on the SWCNT surface. Sodium cholate (SC[10]), sodium deoxycholate

(DOC[11]), sodium dodecyl sulfate (SDS[12]), and sodium dodecylbenzenesulfonate (SDBS[13]) are primarily used to separate SWCNTs by ATPE method. In the classic DEX-PEG system, SC and DOC shift SWCNTs to the bottom phase (dextran-rich), while SDS and SDBS show the opposite effect, promoting the migration of SWCNTs to the upper phase (PEG-rich)[10].

Partitioning of SWCNTs by the ATPE method can also be improved with the use of a modulator, i.e., a compound that is not a phase-forming component or a surfactant, but its presence changes the primary course of separation. Acids[11], bases[14], salts[15], or oxidizing/reducing agents can play such role[16–18].

The ATPE method can be easily adapted - which, together with its simplicity of implementation - were factors that particularly encouraged a more thorough study of this technique. Many papers about ATPE have already been published, demonstrating the successful isolation of SWCNTs by diameter[19], nature of conductivity[17,20], chirality index[14,21] and handedness[11,22].

Aim and scope of the work

This work analysed the process of separation of SWCNTs by ATPE. The obtained results enabled gaining more complete understanding of the mechanism of differentiation. Concomitantly, simple protocols for the selective extraction of specific SWCNTs were developed.

During the study, separation of commercially available mixtures of SWCNTs was undertaken, both having small [**P1, P3, P4**] and large diameters [**P2**].

Contributions [**P1**] and [**P2**] are focused on the analysis of the influence of addition of low molecular weight compounds (so-called modulators) on the course of the extraction process. In the case of [**P1**], these are inorganic salts, while [**P2**] uses a reducing agent (H_2O_2). Works [**P3**] and [**P4**] employed non-ionic surfactants, which had not been previously tested in the separation of SWCNTs by the ATPE method. In [**P3**], the possibility of using single-stranded DNA was also examined.

All the works had the following common features:

- extraction protocol was a one-step method,

- SWCNTs were isolated in a DEX-PEG extraction system containing both components in a 1:1 ratio (m/V),

- prepared volumes of the samples was 1530 μL or multiple of this number,

- the starting materials were prepared as bile salts dispersions.

The use of the same general conditions of separation enabled a precise comparison of the results described in the indicated works.

Separation of carbon nanotubes using aqueous two-phase extraction under basic conditions

In [P1], the influence of alkaline inorganic salts (K_2CO_3, Na_2CO_3, Li_2CO_3, and K_3PO_4) on the isolation result was studied to verify the hypothesis of the influence of pH on the resolution of SWCNT separation by the ATPE method. The starting material synthesized using the HiPco process was solubilized in an aqueous SC solution. Phase-forming polymers (DEX and PEG), SWCNTs dispersion, SDS and SC surfactant solutions, and alkaline salts as modulators were combined.

Regardless of the used salt, it was possible to adjust the system to a attain only one type of SWCNTs - (6,5) SWCNTs - in the bottom phase. It was initially assumed that the pH value is the primary factor, the adjustment of which is necessary to reach favorable separation outcome. However, the measurements showed that depending on the introduced salt, the pH values to achieve the purest (6,5)-SWCNTs are not the same, even considering the measurement error. It was concluded that the tested salts differed in their kosmotropic/chaotropic character, which had a strong effect on the shape of the surfactant micelles, directly affecting the course of the separation.

Subsequent studies also showed that even the extraction of (6,5)-SWCNTs is more complex as (6,5) SWCNTs of different handedness can be detected in the UV-VIS-NIR spectra.

To sum up, [P1] highlighted that tuning the ATPE system can be successfully achieved by introducing low-molecular inorganic compounds. Studies involving a broader spectrum of modulators may reveal more insight into the mechanism of SWCNTs extraction by ATPE method. It is worth noting that the use of highly water-soluble, low-molecular modulators is beneficial while it does not negatively affect the purity of the extracted material The added modulators can be straightforwardly removed by means of simple and low-cost filtration methods.

Generation and thermoelectric characteristics of carbon nanotubes isolated in the presence of hydrogen peroxide

The problem of wasting electricity can be solved by implementing more thermoelectric devices based on the Seebeck effect in everyday life. Semiconducting SWCNTs seem to be a good candidate for use in this type of device, but it is necessary to improve the methods for large-scale harvesting of such species. In [P2], this problem was taken up by separating SWCNTs with large diameters into semiconducting and metallic fractions using the ATPE method.

A system consisting of DEX and PEG was used in this work. The separation was directed using surfactants (SDS and SC), and H_2O_2 was engaged as a partitioning modulator. The extraction protocol was designed to obtain a large amount of material in one step while keeping the concentration of the fractions as high as possible (ensuring that the boundary between the obtained phases can be noticed).

Unfortunately, the isolation of a semiconducting/metallic material does not allow its direct use in thermoelectric devices, because of the impurities introduced during the separation step. In order to remove the non-essential components contaminating the SWCNTs, novel purification methods have been developed based on thermal desorption and hydrolysis (in the case of fractions collected from Dextran). The purity of the materials was gauged by thermogravimetric analysis and scanning electron microscopy.

The purified fractions and the starting material (as a reference) were used to prepare thin films by vacuum filtration. Next, electrical conductivity and the Seebeck coefficients of as-prepared thin SWCNT films were measured in the temperature range between 40 and 110℃. Among the tested materials, the semiconducting fraction was generally characterized by the best Seebeck coefficient and the lowest electrical conductivity.

The methodology designed in [P2] reports a large-scale separation of the material and describes new more effective method of SWCNT purification from contaminants such as polymers and surfactants.

Purification of carbon nanotube mixtures facilitated by non-ionic surface active compounds

The research described in [P3] involves the use of a non-ionic surfactant - Pluronic F127 (PL127), which has not yet been tested in the context of separation SWCNTs. PL127 is a copolymer of ethylene and propylene glycol that can act as a co-surfactant against SC in the extraction system consisting of DEX and PEG.

For detailed investigation of the influence of PL127 on SWCNT partitioning, two types of starting materials were used - one was enriched in (6,5) chirality, while the other contained a broad distribution of SWCNT types. During the study, the impact of PL127, SC and the influence of the composition of starting material on the separation were investigated. Changes in the composition of the separated phases were thoroughly monitored using high-throughput photoluminescence spectroscopy (PL). It was noticed that PL127 shifted SWCNTs to the less hydrophilic upper phase (rich in PEG), while the SC showed the opposite behavior. The analysis of changes in species distribution showed that the separation using PL127 and SC follows the pattern wherein SWCNTs migrate to the top phase, starting with those with the largest diameters. Conversely, when the material was initially deposited in the top phase (by applying appropriate PL127/SC ratio), the migration to the bottom phase occurred in order from the smallest diameters, which was driven by the addition of SC. Detailed analysis of the partitioning system was beneficial, as it enabled the possibility of isolating pure fractions of (7,5)- or (6,5)-SWCNTs, in the upper or lower phase, respectively.

Research reported in [P3] has also been extended and SWCNTs dispersed with single-stranded DNA were also examined. The purity of such raw material was also considerably improved by ensuring appropriate amounts of PL127 and SC in the ATPE system. The obtained results are important because as-collected chirality-defined SWCNT materials are highly useful in biomedical applications.

High resolution differentiation of carbon nanotubes using aqueous two-phase extraction modulated and mixtures of ionic and non-ionic surfactants

In [P4], more attention was devoted to study the effect of non-ionic surfactants on the separation of SWCNTs by the ATPE method. Triton X-100 (TX-100) was chosen as a model compound.

First, TX-100 was tested as a cosurfactant against DOC, but the excessive strength of the latter was noted, resulting in the retention of most of the SWCNTs in the lower phase, which discouraged deeper study using these compounds. Changing DOC to SC turned out to be effective and allowed precise observation of the course of separation, which, as it turned out, followed the diameter order. In addition, (6,4) SWCNTs (the smallest among semiconducting SWCNTs in the material) were isolated across a large concentration range of non-ionic surfactant as a monochiral fraction. The developed methodology was highly effective, enabling the separation of (6,4)-SWCNTs from all commercially available mixtures of SWCNTs, including the material produced by the HiPco method, where the mentioned species is available in negligible small amount.

A similar course of separation was observed for other non-ionic surfactants, differing in physical/chemical properties and structure. In order to understand the phenomena promoting such separation mechanism, the experimental results were complemented with modeling concerning e.g. adsorption energy of a surfactant molecule on the surface of SWCNTs and the rate of surfactant corona formation. Computations clearly showed that non-ionic surfactants adsorb more easily on SWCNTs with larger diameters. Moreover, it was observed that they displace water from the SWCNT surface, thereby making the material more hydrophobic. Consequently, due to these two effects, SWCNT migrate to the less hydrophilic top phase, starting from the largest species present in the raw material.

The work described in [P4] presents the benefits of application of non-ionic surfactants for SWCNT purification that have a strong affinity for SWCNTs with large diameters. This phenomenon is likely not limited to the ATPE method, so other separation techniques may capitalize on the findings reported in this contribution.

Conclusions

This works presented in the dissertation show that effective separation of SWCNTs using the ATPE method is possible based on simple and repeatable one-step protocols. Proposed methods are based on easily available reagents and are scalable, so their application on a semi-industrial scale is probable.

By selecting the appropriate modulator and its concentration, it is possible to reach process conditions favoring the isolation of monochiral fractions such as (6,4), (6,5) or (7,5), which have a high application potential in photovoltaics or medical imaging. Moreover, the raw material can be separated according to the nature of conductivity, delivering valuable material for microelectronics and telecommunications.

Surfactants play the key role in the separation of SWCNTs by ATPE. Nonetheless, the mechanism of this process multidimensional, so a series of experiments was required to gain a sufficient insight into the ATPE mechanism. [P1], [P3], and [P4] contributions revealed a number of details about the underlying phenomena. Still, the discovery of the action of non-ionic surfactants described in [P4], which was explained using modelling, gave the clearest view of the interactions between SWCNTs and the components of the two-phase system.

Currently, based on the experience from articles [P1-P4], subsequent work is underway to fully unravel the mechanism of the ATPE system, taking into account more factors such as the density of used chemical reagents, the hydrophilicity of the phases, and the characteristics of the sorted mixtures of SWCNTs.

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Contributions

I assess my contribution to the following articles to be:

- [P1]: 60%

- [P2]: 55%

- [P3]: 55%

- [P4]: 50%

Justification: In these works, I was a co-author of research concepts, conducted experiments, processed data, performed a preliminary interpretation of the obtained results, prepared a draft of the manuscripts, and participated in further work on them until the level of the papers was acceptable by the publisher.