

Single-walled carbon nanotubes fractionation via electrophoresis

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This work presents the influence of the sonication time on the efficiency of the metallic/semiconducting (M/S) fractionation of diazonium salt functionalized single-walled carbon nanotubes (SWCNTs) via free solution electrophoresis (FSE) method. The SWCNTs synthesized via laser ablation were purified from amorphous carbon and catalyst particles through high vacuum annealing and subsequent refluxing processes in aqua regia solutions, respectively. The purified material was divided into two batches. The SWCNTs samples were dispersed in 1% SDS solution in ultrasound bath for 2 and 12 hours. Both dispersed SWCNTs samples were functionalized with p-aminobenzoic acid diazonium salt and fractionated via free solution electrophoresis method. Afterwards, the fractionated samples were recovered, purified from surfactant/functionalities by annealing and investigated via UV-Vis-NIR optical absorption spectroscopy (OAS). The efficiency of the fractionation process was estimated through the comparison of the van Hove singularities (vHS) presented in the obtained fractions to the starting SWCNTs.

Keywords: SWCNTs, diazonium salts, fractionation, electrophoresis.

INTRODUCTION

Carbon nanotubes (CNTs) were observed in 1991 by Japanese scientist Sumio Iijima¹. However, other sources point earlier observations by Russian researchers L. V. Radushkevich and V. M. Lukyanovich². Single-walled carbon nanotubes (SWCNTs) due to their nanometer size, optical and electrical properties have great potential for further miniaturisation of the electronic devices. According to their chirality, SWCNTs can act as conductors or as semiconductors^{3, 4}. As produced CNTs contain different types of tubes with different electric conductivity which is limiting the further industrial applications. The typical synthesized material contains approximately 30% of metallic and 70% of semiconducting tubes.

In order to obtain material for application in nanoelectronic field, the sample should be fractionated to its electrical counterparts. The first step of the preparation is the purification process, which removes the amorphous carbon together with fullerenes previously formed during the synthesis process^{5, 6, 7}. The as-produced material exhibits strong hydrophobic properties, which result in rapid agglomeration into the bundles when exposed to water environment. In order to obtain stable suspension of individual tubes and improve their hydrophilic behaviour, the second step involves an employment of the surface agents or the introduction of the functional groups such as: -OH, -COOH, -NH₂ onto outer walls. The final step of CNTs preparation is the fractionation process.

The chemical methods of nanotubes fractionation are based on the affinity of certain molecules to only one type of tubes, e.g. selective destruction of semiconducting nanotubes via hydrogen peroxide treatment, which results in sample enrichment in metallic CNTs⁸. Other chemical fractionation method is the selective dispersion in organic solvents or surfactants solutions⁹. The nanotubes exhibit different electrical properties, therefore surfactant is attached with different force and rate. The nanotubes with higher concentration of the surfactants on the sidewalls are dispersed readily and they undergo debundling rela-

tively easy¹⁰. In the nanotubes fractionation field, the physical CNTs properties are used in methods such as: density gradient ultracentrifugation¹¹, chromatography¹² and electrophoresis techniques¹⁰.

Electrophoretical fractionation process is based on migration of the macromolecules in the electric field depending on their mass, charge or isoelectric point. Considering the fact that pristine purified nanotubes are chemically inert, the electric charge have to be granted via non-covalent or covalent sidewall modification to separate nanotubes via electrophoretical process. A non-covalent functionalisation of the nanotubes can be carried out by attaching to their walls cationic or anionic surfactants via the adsorption process. Sodium dodecyl sulphate (SDS) is a surface active agent commonly used in electrophoresis processes and can selectively disperse single-walled nanotubes. SDS molecules attach to both types of SWCNTs, however with different ratio depending on the type of tubes. This dependence allows to separate SWCNTs according to their metallic character. Other approach which grants electric charge to the CNTs surface is covalent functionalisation via the diazonium salt grafting. This process is selective method. The metallic SWCNTs have greater chemical affinity to diazonium salts than the semiconducting ones and therefore the metallic/semiconducting fractionation can be performed¹⁰.

Basing on the type of electrophoresis apparatus and electrophoretical medium there are different types of electrophoresis such as capillary electrophoresis, zone electrophoresis, isoelectric focussing, free solution electrophoresis (FSE) and the others¹³. This contribution presents study on the influence of the sonication time on FSE fractionation of the covalently functionalized SWCNTs. We tested the p-aminobenzoic acid diazonium salts functionalized SWCNTs.

EXPERIMENTAL

Hydrochloric acid 35%–38% p.a., nitric acid 65% p.a., acetone 99.5% p.a., diethyl ether 99.5% p.a., sodium phosphate p.a. and disodium phosphate p.a. were purchased from Chempur. 4-Aminobenzoic acid – $\geq 98.0\%$ (HPLC/NT) was obtained from Fluka. Sodium dodecyl sulfate – for electrophoresis, $\geq 98.5\%$ (GC) and Triton® X-100 for electrophoresis were purchased from Sigma. Acetonitrile – anhydrous, 99.8% was obtained from Sigma-Aldrich. Nitrosyl tetrafluoroborate – 95% was purchased from Aldrich. All the solutions were based on RO H₂O (type II water obtained in reversed osmosis process with conductance $0.056 \mu\text{S cm}^{-1}$).

Single-walled carbon nanotubes used for this experiment were produced via laser ablation¹⁴. In the first step of the purification, the raw material underwent the initial annealing process at 600 °C under vacuum conditions (10^{-5} mbar) for 4 hours to remove the amorphous carbon. The remaining catalyst particles were removed by tripled acid treatment at 175°C in quadrupled diluted aqua regia (HCl:HNO₃ 3:1) solution for 24 hours in total. After catalyst removal, the sample was filtered through the polycarbonate filter (Whatman pore size $0.2 \mu\text{m}$) and rinsed thoroughly with ROH₂O and acetone. Finally, in order to remove introduced oxygen functional groups, the purified sample was annealed at 1100 °C in vacuum (10^{-5} mbar) for 1 hour. Reference SWCNTs material was dispersed in phosphate buffer at ultrasound bath (300 W, 40 kHz). Next, the sample was divided into two batches of known amount of the material. In order to exfoliate (debundle) the nanotubes bundles, the first and the second batch underwent 2 and 12 hours of the ultrasonication in 1% SDS solution. Next, the dispersed nanotubes were functionalised with p-aminobenzoic diazonium salt. The experimental details of the p-aminobenzoic acid diazonium salt synthesis process is described elsewhere¹⁵. The nanotube suspensions were heated to 45°C. In 30 min time intervals $25 \mu\text{l}$ of salt solution was added until reaching 0.04 mM salt concentration. The reaction was conducted for 12 hours with assistance of the magnetic stirrer. After the functionalization, the samples were filtered through the polycarbonate filter (Whatman pore size $0.2 \mu\text{m}$) and rinsed thoroughly with ROH₂O and acetone. The as-prepared samples were dispersed in Triton-X ($\sim 2 \mu\text{g}$ of SWCNT in 1 ml of 2% Triton X 405) for 45 min in ultrasound bath.

The prepared samples underwent electrophoresis in 0.1 M phosphate buffer solution (pH 7.5). Electrophoresis was proceeded for 24 hours at 150 V. This process was performed in a custom-made glass chambers connected via glass tube (diameter 9 mm, length 120 mm) with inlet port placed at the centre of glass tube and two platinum electrodes placed in each chamber. After the fractionation process two fractions were collected. The migrating fraction was collected from electrode area. The control fraction was collected from inlet port area. To remove adsorbed surfactant and introduced functional groups the samples of collected fractions were annealed at 600 °C in high vacuum (10^{-5} mbar) for 4 hours. Afterwards, the annealed fraction samples were dispersed in acetone at ultrasound bath and subsequently sprayed on quartz plates via drag and drop method on the hot plate.

In order to observe the changes in van Hove singularities in the samples before and after the fractionation processes, the optical absorption spectra (OAS) in the range UV-Vis-NIR were performed using Jasco V-570. The morphology of the starting material was investigated on a high resolution transmission electron microscope (HRTEM) [FEI Tecnai F30].

RESULTS AND DISCUSSION

Optical properties of CNTs derive from electronic transitions within one-dimensional density of states (DOS). The pronounced peaks, which can be observed in optical absorption spectra of the one-dimensional structures in the range of UV-Vis-NIR, are called van Hove singularities (vHS). The energy of the van Hove singularities depends on the nanotube structure/diameter. However, the diameter distribution of the tubes in the sample should be relatively narrow. In the case of the sample with broad diameter distribution vHS are smeared out. In this study SWCNTs exhibit diameter distribution in the range between 2–1.3 nm. Typical bundles of the starting pristine tubes are shown in figure 1.

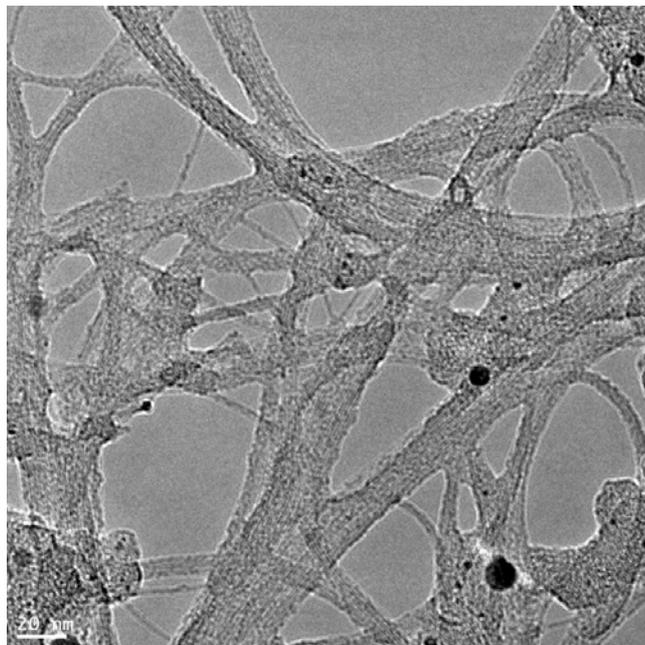


Figure 1. HR-TEM image of the starting pristine SWCNT bundles

Figure 2 presents the typical optical absorption spectra of single-walled carbon nanotubes in the range of UV-Vis-NIR. The peaks corresponding to the metallic (EM11) and semiconducting SWCNTs (ES11, ES22) are distinguished¹⁷. The insert of this figure presents the equation used for the estimation of the metallic nanotubes content in the sample¹⁶. Diazonium salt functionalisation of the SWCNTs influences the optical properties of nanotubes leading to disappearance of the van Hove singularities in OAS spectrum (data not shown here)¹⁸. However, the application of the thermal process defunctionalize the sample and the full restoration of the van Hove singularities occurred. This allows the estimation of the metallic tubes content in the investigated samples.

Figures 3 and 4 present OAS spectra of the annealed samples sonicated in SDS for 2 and 12 hours, respectively.

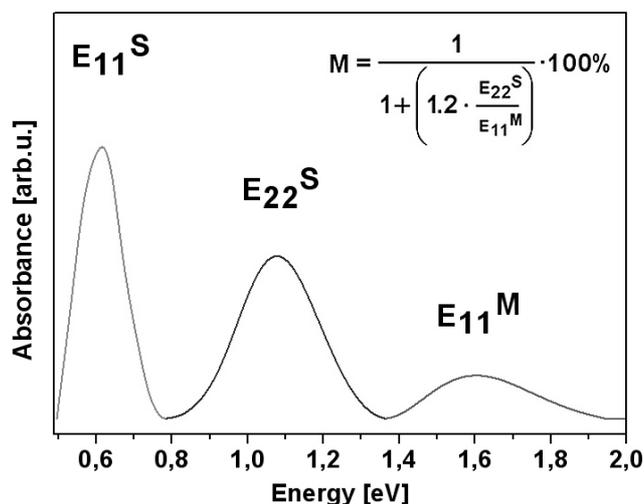


Figure 2. OAS spectrum of SWCNTs. Equation used for the estimation of metallic tubes content

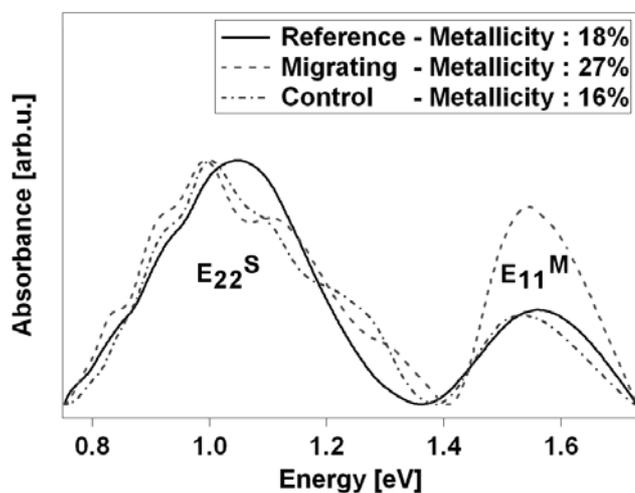


Figure 3. OAS spectra of samples after 2 hours of sonication

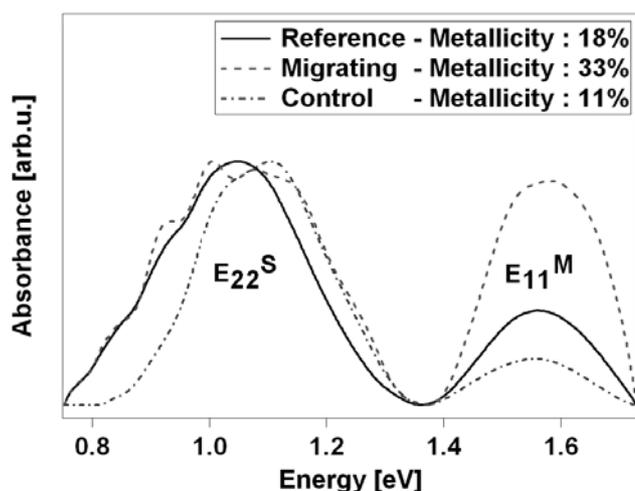


Figure 4. OAS spectra of samples after 12 hours of sonication

In the figures 3 and 4, it can be observed that the area under metallic peaks significantly increased (from 18% in a reference material, up to 27% and 33% for 2 and 12 hours of sonicated samples, respectively) in both migrating fractions. Additionally, the area under the control fractions decreased (to 16% and 11% for 2 and 12 hours of sonicated samples, correspondingly). Comparing the

migrating fractions (figures 3, 4) of sonicated samples for 2 and 12 hours, it can be noticed the enhanced functionalisation of the nanotubes induced by longer sonication (12 hours) prior the reaction with diazonium salt. Therefore, the concentration of the metallic tubes in this sample is higher than in the sample sonicated for 2 hours. This is related to two main effects: the prolonged sonication process leads to better exfoliation and exposure of the CNTs sidewalls to the diazonium salt, and the SDS disperses metallic nanotubes more efficiently than semiconducting ones.

Tanaka et. al. reported the gel electrophoresis of nanotubes for fractionation of metallic and semiconducting counterparts¹⁹. The fractionation yield was surprisingly high (~70% of metallic SWCNT in the final sample) in comparison to presented free solution electrophoresis process (15%). However, this technique suffers very important barrier, namely the difficulty to remove the agarose gel from the separated sample. In case of free solution electrophoresis there is no need to apply the gel and the sample is easily cleaned from the surfactants and functional groups via efficient high temperature annealing procedure. Therefore, after the appropriate optimization it could be scaled up in M/S fractionation of SWCNTs.

CONCLUSION

Summarizing, the influence of the sonication time of the SWCNTs in SDS solution on the efficiency of the M/S fractionation was investigated. Longer exposure to ultrasounds leads to more efficient exfoliation of the CNTs bundles what leads to the higher functionalization degree. It can be clearly seen that higher functionalisation yield is related to the prolonged sonication treatment of the samples and therefore more efficient fractionation is detected. In order to optimize the separation yield, different diazonium salt concentration will be employed.

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