

Separation of semi-conducting and metallic single-walled carbon nanotubes using a polytungstate

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(71) Applicant: **BASF SE** [DE/DE]; Carl-Bosch-Strasse 38,
67056 Ludwigshafen am Rhein (DE).

(72) Inventors: **TOMOVIC, Zeljko**; Elastogranstraße 60,
49448 Lemförde (DE). **REIS, Wieland**; Schleifweg 7,
69126 Heidelberg (DE). **MIKHAEL, Jules**; Carl-Bosch-
Strasse 38, 67056 Ludwigshafen (DE).

(74) Agent: **BASF IP ASSOCIATION**; BASF SE, G-FLP -
C006, 67056 Ludwigshafen (DE).

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(54) Title: SEPARATION OF SEMI-CONDUCTING AND METALLIC SINGLE-WALLED CARBON NANOTUBES USING A POLYTUNGSTATE

(57) Abstract: The present invention relates to a method for separating semi-conducting and metallic single-walled carbon nanotubes from each other and, if present, from other carbonaceous material, or for separating semi-conducting single-walled carbon nanotubes from other carbonaceous material, via centrifugation performed by a temperature of > 25°C using a solution of a polytungstate as separation medium; to semi-conducting single-walled carbon nanotubes obtainable by this method; and to the use of these semi-conducting single-walled carbon nanotubes e.g. in electronic devices, optical devices, optoelectronic devices, energy storage devices and the like.



WO 2018/099774 A1

Separation of semi-conducting and metallic single-walled carbon nanotubes using a polytungstate

Description

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The present invention relates to a method for separating semi-conducting and metallic single-walled carbon nanotubes from each other and, if present, from other carbonaceous material, or for separating semi-conducting single-walled carbon nanotubes from other carbonaceous material via a centrifugation step performed at a temperature of $> 25^{\circ}\text{C}$ using a solution of a polytungstate; to semi-conducting single-walled carbon nanotubes obtainable by this method; and to the use of these semi-conducting single-walled carbon nanotubes e.g. in electronic devices, optical devices, optoelectronic devices, energy storage devices and the like.

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure and are members of the fullerene structural family. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, i.e. by graphene. These sheets are rolled at specific and discrete ("chiral") angles, and the combination of the rolling angle and radius decides the nanotube properties; for example, whether the individual nanotube shell shows a metal or semiconductor behavior. Carbon nanotubes are generally categorized as single-walled carbon nanotubes (SWCNTs; often just SWNTs) and multi-walled carbon nanotubes (MWCNTs; often just MWNTs).

The structure of an SWNT can be conceptualized by wrapping a one-atom-thick layer of graphene into a seamless cylinder. As a result of this structure, SWNTs are available in a large number of different chiralities due to various combinations of diameter and wrapping angle. The nanotube chirality defines both its electronic and optical properties, and hence is a critical parameter when incorporating nanotubes into device applications. For instance, roughly two thirds of SWNT chiralities are semiconducting, while the rest are of metallic nature. Moreover, the first-order peaks in optical absorbance for metallic SWNTs can vary widely from about 400 nm to 800 nm as SWNT diameter is increased from 0.7 nm to 1.8 nm. Although this striking dependence between SWNT atomic structure and behavior enables them to be employed in many ways, it is also regarded as one of their major weaknesses, as so far there are no practical methods of synthesizing SWNTs of uniform chirality. Instead, as-synthesized SWNTs typically consist of a mixture of semiconducting and metallic nanotubes with varying diameters. Methods for the synthesis of CNTs are arc discharge, laser ablation, high-pressure carbon monoxide disproportionation (also termed high pressure CO conversion; HiPCO), plasma torch, aerosol synthesis, chemical vapor deposition (CVD) and combinations thereof.

The slight difference in the angle at which semiconducting and metallic nanotubes are rolled up into a seamless cylinder also results in subtle differences in density. These different densities

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are the general principle for separating semiconducting and metallic nanotubes. The buoyant densities of SWNTs in aqueous solution subtly depend on factors such as the mass and volume of the SWCNT itself, its surface functionalization and charge, coverage with surface-active compounds and electrostatically bound hydration layers. The differences in the buoyant densities result into different positions of the SWNTs within a density gradient medium when they are subjected to high centripetal forces.

In the separation methods so far used, either both electrical types of SWNTs (semi-conducting and metallic) are functionalized with standard surfactants, such as sodium cholate or sodium dodecyl sulfate, or just one type, mostly the semi-conducting SWNT, is functionalized with specific additives. This (partial) functionalization enhances the difference in the densities of the various SWNT types. The (partly) functionalized SWNTs are then subjected to a density gradient ultracentrifugation (DGU). Under high gravitational forces the nanomaterials are driven by density differences to positions where their buoyant density is equal to that of the surrounding fluid (isopycnic point). Density gradient media so far used for SWCNT separation are aqueous solutions of sugar(-like) molecules, such as sucrose, polysucrose, Nycodenz® (5-(N-2,3-dihydroxypropylacetamido)-2,4,6-tri-iodo-N'-bis(2,3-dihydroxypropyl)isophthalamide; iohexol) or iodixanol (5-{N-[3-(N-{3,5-bis[(2,3-dihydroxypropyl)carbamoyl]-2,4,6-triiodophenyl]-acetamido)-2-hydroxypropyl]acetamido}-1-N,3-N-bis(2,3-dihydroxypropyl)-2,4,6-triiodobenzene-1,3-dicarboxamide). Another density gradient medium used for SWCNT separation is Percoll® (GE Healthcare), which consists of colloidal silica particles of 15-30 nm diameter (23% w/w in water) coated with polyvinylpyrrolidone.

M.S. Arnold, A.A. Green, J.F. Hulvat, S.I. Stupp and M.C. Hersam describe in Nature Nanotechnology, 2006, 1, 60-65 the separations of CNTs by density gradient ultracentrifugation at a temperature of 22°C. Sodium dodecyl sulfate, sodium dodecyl benzene sulfonate, sodium cholate, sodium deoxycholate and sodium taurodeoxycholate are used for dispersing/functionalizing the nanotubes. The density medium is an aqueous solution of iodixanol.

US 2012/025150 A1 deals also with separation of CNTs by density gradient ultracentrifugation at a temperature of 22°C using poly(ethyleneoxide)-(polypropyleneoxide) block-co-polymers as surfactants.

A.L. Antaris, J.-W. T. Seo, A.A. Green and M.C. Hersam describe in ACSNano, 2010, 4(8), 4725-4732 the separations of CNTs by non-linear density gradient centrifugation using Pluronics® (linear copolymers with a central polypropylene oxide (PPO) block flanked by two polyethylene (PEO) blocks) and Tetronics® (X-shaped copolymers with four PPO-PEO blocks bonded to a central ethylene diamine linker) as surfactants and an aqueous solution of iodixanol as density medium.

S. Ghosh, S.M. Bachilo and R.B. Weisman describe in Nature Nanotechnology, 2010, 5(6), 443-450 the separations of CNTs by non-linear density gradient centrifugation. The density medium is an aqueous solution of iodixanol further containing the surfactant sodium cholate. This surfactant is also used for dispersing/functionalizing the nanotubes.

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K. Yanagi, T. Iitsuka, S. Fujii and H. Kataura, J. Phys. Chem. 2008, 112, 11889-18894 use sucrose as density medium.

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A.A. Green and M.C. Hersam, Advanced Materials 2011, 23, 2185-2190 produce nearly single-chirality single-walled CNTs via orthogonal iterative DGU using sodium dodecyl sulfate in combination with sodium cholate as surfactants and iodixanol as density medium.

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Homenick et al, J. Phys. Chem C, 2014, describes the use of block copolymers in density gradient ultracentrifugation. It is disclosed that lowering the temperature below 10°C during the DGU separation results in higher purity and yield.

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WO 2016/024196 describes the separation of CNTs via density gradient centrifugation by using a semiconducting polymer as surfactants. It is disclosed that the centrifugation is preferably performed in the temperature range of 10 to 20°C.

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The disadvantage of the separation methods of the prior art is the laborious, time-consuming preparation of the density gradients. In addition, when semiconducting polymer is used as surfactant expensive catalysts are needed for the synthesis of such polymers, and toxic aromatic or heteroaromatic solvents are used. Furthermore, the separation step can be done only at very low concentration of CNTs such as 0.01 wt.-%. Moreover, satisfactory separations are only obtained after protracted centrifugation times and require high rotational speeds (e.g. 55,000 rpm or 300,000 x g). The resulting bands containing the enriched SWNT forms are often small and diffuse and thus very difficult to separate. This impedes separation on a higher scale. Also, the viscosity sharply increases with increasing concentration of the density gradient medium. A high

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viscosity hampers the movement of the nanomaterials to their corresponding isopycnic point, which makes the separation methods of the prior art particularly time-consuming. In addition, these high rotational speeds, above 15,000 x g, are not yet suitable for large-scale technological processes.

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WO 2016/046153 discloses a successful separation of CNTs using room-temperature centrifugation with moderate rotational speeds of 10,000 x g. The term "room-temperature" is generally accepted to refer to an actual temperature between 18 and 25 °C. It is disclosed that the separation could be done by using polyarylether as surface-active compound in a solution of polytungstate. Therefore, WO 2016/046153 discloses a process suitable for large-scale technological processes.

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Since electronic applications require predictable and uniform performance, strategies are sought for effective post synthesis separation of SWCNTs.

The identification of scalable processes that transfer random mixtures of single-walled carbon nanotubes into fractions featuring a high content of semiconducting species is therefore crucial for future application of SWCNTs in high-performance electronics. Highly integrated circuits and or CPUs consist of 100 million to a billion transistors. In order to show the superior intrinsic semiconductor properties of SWCNTs the failure rate has to be minimized. This means that SWCNTs have to be in the highest possible semiconducting purity to compete with existing semiconductor technology and thus, getting highest possible semiconducting purity is an ongoing task in this technical field.

The object of the present invention was to provide a method for separating semi-conducting single-walled carbon nanotubes from other carbonaceous material, in particular from metallic single-walled carbon nanotubes, which is simpler, less tedious and less energy- and/or time-consuming than the prior art methods, especially the prior art using high rotational speeds or DGU. In addition, the process should be suitable for large-scale technological processes. In addition, the process should yield the highest purity semi-conducting single-walled carbon nanotubes.

Surprisingly, the performance of the centrifugation step, whereas the centrifugation is performed at a temperature of $> 25^{\circ}\text{C}$ and using a solution of polytungstates, especially SPT, as a separation medium, proved to be a useful separation method which results in high purity semi-conducting single-walled carbon nanotubes. In addition, the time period of centrifugation could be reduced in comparison to room-temperature centrifugation.

The invention thus relates to a method for separating semi-conducting single-walled carbon nanotubes from metallic single-walled carbon nanotubes and, if present, from other carbonaceous material, or for separating semi-conducting single-walled carbon nanotubes from other carbonaceous material, whereas method comprises bringing a composition containing semi-conducting and metallic single-walled carbon nanotubes and optionally other carbonaceous material, or a composition containing semi-conducting carbon nanotubes and other carbonaceous material, into contact with at least one surface-active compound and with a solution of a polytungstate, and subjecting the obtained composition to a centrifugation step, whereas the centrifugation is performed at a temperature of $> 25^{\circ}\text{C}$.

Conducting the present invention, the obtained nanotubes are also separated from metal oxide impurities and catalyst particles (e.g. Fe, Co, Ni, etc.) used for synthesis of CNTs, which remain after production of the CNTs.

The invention thus relates in one aspect to a method for separating semi-conducting and metallic single-walled carbon nanotubes from each other and, optionally and if present, from other carbonaceous material, metal oxide impurities and/or catalyst particles, or for separating semi-

conducting single-walled carbon nanotubes from other carbonaceous material, metal oxide impurities and/or catalyst particles, whereas method comprises bringing a composition containing semi-conducting and metallic single-walled carbon nanotubes and optionally other carbonaceous material, metal oxide impurities and/or catalyst particles, or a composition containing
5 semi-conducting carbon nanotubes and other carbonaceous material, metal oxide impurities and/or catalyst particles, into contact with at least one surface-active compound and with a solution of a polytungstate, and subjecting the obtained composition to a centrifugation step, whereas the centrifugation is performed at a temperature of $> 25^{\circ}\text{C}$.

10 In another aspect, the invention thus relates to a method for separating semi-conducting and metallic single-walled carbon nanotubes from each other and, optionally and if present, from other carbonaceous material, whereas method comprises bringing a composition containing semi-conducting and metallic single-walled carbon nanotubes and optionally other carbonaceous material into contact with at least one surface-active compound and with a solution of a
15 polytungstate, and subjecting the obtained composition to a centrifugation step, whereas the centrifugation is performed at a temperature of $> 25^{\circ}\text{C}$.

In another aspect, the invention relates to a method for separating semi-conducting single-walled carbon nanotubes from other carbonaceous material, whereas method comprises bringing
20 a composition containing semi-conducting carbon nanotubes and other carbonaceous material, in particular metallic single-walled carbon nanotubes, into contact with at least one surface-active compound and with a solution of a polytungstate, and subjecting the obtained composition to a centrifugation step, whereas the centrifugation is performed at a temperature of $> 25^{\circ}\text{C}$.

25 In another aspect, the invention thus relates to a method for separating semi-conducting single-walled carbon nanotubes from metal oxide impurities and/or catalyst particles, whereas method comprises bringing a composition containing semi-conducting single-walled carbon nanotubes and metal oxide impurities and/or catalyst particles into contact with at least one surface-active compound and with a solution of a polytungstate, and subjecting the obtained composition to a
30 centrifugation step, whereas the centrifugation is performed at a temperature of $> 25^{\circ}\text{C}$.

The invention thus also relates to a method for obtaining semi-conducting single-walled carbon nanotubes, whereas method comprises bringing a composition containing semi-conducting single-walled carbon nanotubes and undesired carbonaceous material into contact with at least
35 one surface-active compound and then with a solution of a polytungstate, and subjecting the obtained composition to a centrifugation step, whereas the centrifugation is performed at a temperature of $> 25^{\circ}\text{C}$.

The method of the invention using a polytungstate as a separation medium can be used for obtaining either preferentially semi-conducting single-walled carbon nanotubes or both semi-conducting and metallic single-walled carbon nanotubes. In a preferred embodiment, however, the method of the invention serves for obtaining semi-conducting single-walled carbon nanotubes.

5 The organic moieties mentioned in the below definitions of the variables are - like the term halogen - collective terms for individual listings of the individual group members. The prefix C_n-C_m indicates in each case the possible number of carbon atoms in the group.

10 The term halogen denotes in each case fluorine, bromine, chlorine or iodine, in particular fluorine, chlorine or bromine.

The term "alkyl" as used herein and in the alkyl moieties of alkoxy, alkylthio, alkylsulfonyl, alkyl-carbonyl, alkoxy-carbonyl etc. refers to saturated straight-chain or branched hydrocarbon radi-
15 cals having 1 to 4 ("C₁-C₄-alkyl") or 1 to 10 ("C₁-C₁₀-alkyl") or 1 to 20 ("C₁-C₂₀-alkyl") or 10 to 20 ("C₁₀-C₂₀-alkyl") or 2 ("C₂-alkyl") or 2 to 3 ("C₂-C₃-alkyl") or 2 to 5 ("C₂-C₅-alkyl") carbon atoms. C₁-C₄-Alkyl is methyl, ethyl, n-propyl, isopropyl, n-butyl, 1-methylpropyl (sec-butyl), 2-methylpropyl (isobutyl) or 1,1-dimethylethyl (tert-butyl). C₁-C₁₀-Alkyl is additionally also, for example, pen-
20 tyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dime-
thylpropyl, 1,2-dimethylpropyl, hexyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-
methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-di-
methylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trime-
thylpropyl, 1-ethyl-1-methylpropyl, 1-ethyl-2-methylpropyl, heptyl, octyl, 2-ethylhexyl, nonyl,
25 decyl and positional isomers thereof. C₁-C₂₀-Alkyl is additionally also, for example, undecyl, do-
decyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl and
positional isomers thereof. Examples for C₁₀-C₂₀-alkyl are decyl, undecyl, dodecyl, tridecyl,
tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl and positional iso-
mers thereof. C₂-Alkyl is ethyl. C₂-C₃-Alkyl is ethyl, n-propyl or isopropyl. C₂-C₅-Alkyl is addition-
30 ally also, for example, n-butyl, 1-methylpropyl (sec-butyl), 2-methylpropyl (isobutyl), 1,1-di-
methylethyl (tert-butyl), pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl,
1-ethylpropyl, 1,1-dimethylpropyl or 1,2-dimethylpropyl.

The term "haloalkyl" as used herein refers to straight-chain or branched alkyl groups having 1 to
35 4 ("C₁-C₄-haloalkyl") carbon atoms (as mentioned above), where some or all of the hydrogen
atoms in these groups are replaced by halogen atoms as mentioned above. Examples are
chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluo-
romethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromo-
ethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-
chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl, 1-

fluoropropyl, 2-fluoropropyl, 3-fluoropropyl, 1,1-difluoropropyl, 2,2-difluoropropyl, 1,2-difluoropropyl, 3,3-difluoropropyl, 3,3,3-trifluoropropyl, heptafluoropropyl, 1,1,1-trifluoroprop-2-yl, 3-chloropropyl, 4-chlorobutyl and the like.

- 5 C₁-C₄-Hydroxyalkyl is a C₁-C₄-alkyl group as defined above wherein one of the hydrogen atoms is replaced by an OH group. Examples are hydroxymethyl, 1-hydroxyethyl, 2-hydroxyethyl, 1-hydroxypropyl, 2-hydroxypropyl, 3-hydroxypropyl, 1-hydroxy-1-methylethyl, 2-hydroxy-1-methylethyl, 1-hydroxybutyl, 2-hydroxybutyl, 3-hydroxybutyl, 4-hydroxybutyl and the like.
- 10 The term "C₁-C₄-alkoxy" is a C₁-C₄-alkyl group, as defined above, attached via an oxygen atom. The term "C₁-C₁₀-alkoxy" is a C₁-C₁₀-alkyl group, as defined above, attached via an oxygen atom. C₁-C₄-Alkoxy is methoxy, ethoxy, n-propoxy, 1-methylethoxy (isopropoxy), butoxy, 1-methylpropoxy (sec-butoxy), 2-methylpropoxy (isobutoxy) or 1,1-dimethylethoxy (tert-butoxy). C₁-C₁₀-Alkoxy is additionally, for example, pentoxy, 1-methylbutoxy, 2-methylbutoxy, 3-methyl-
- 15 butoxy, 1,1-dimethylpropoxy, 1,2-dimethylpropoxy, 2,2-dimethylpropoxy, 1-ethylpropoxy, hexoxy, 1-methylpentoxy, 2-methylpentoxy, 3-methylpentoxy, 4-methylpentoxy, 1,1-dimethylbutoxy, 1,2-dimethylbutoxy, 1,3-dimethylbutoxy, 2,2-dimethylbutoxy, 2,3-dimethylbutoxy, 3,3-dimethylbutoxy, 1-ethylbutoxy, 2-ethylbutoxy, 1,1,2-trimethylpropoxy, 1,2,2-trimethylpropoxy, 1-ethyl-1-methylpropoxy, 1-ethyl-2-methylpropoxy, heptyloxy, octyloxy, 2-ethylhexyloxy, nonyloxy,
- 20 decyloxy and positional isomers thereof.

The term "C₁-C₄-haloalkoxy" is a C₁-C₄-haloalkyl group, as defined above, attached via an oxygen atom. C₁-C₄-Haloalkoxy is, for example, OCH₂F, OCHF₂, OCF₃, OCH₂Cl, OCHCl₂, OCCl₃, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2-bromoethoxy, 2-iodoethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy, OC₂F₅, 2-fluoropropoxy, 3-fluoropropoxy, 2,2-difluoropropoxy, 2,3-difluoropropoxy, 2-chloropropoxy, 3-chloropropoxy, 2,3-dichloropropoxy, 2-bromopropoxy, 3-bromopropoxy, 3,3,3-trifluoropropoxy, 3,3,3-trichloropropoxy, OCH₂-C₂F₅, OCF₂-C₂F₅, 1-(CH₂F)-2-fluoroethoxy, 1-(CH₂Cl)-2-chloroethoxy, 1-(CH₂Br)-2-bromoethoxy, 4-fluorobutoxy, 4-chlorobutoxy, 4-bromobutoxy or nonafluorobutoxy.

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The term "C₁-C₄-alkylthio" is a C₁-C₄-alkyl group, as defined above, attached via a sulfur atom. C₁-C₄-Alkylthio is methylthio, ethylthio, n-propylthio, 1-methylethylthio (isopropylthio), n-butylthio, 1-methylpropylthio (sec-butylthio), 2-methylpropylthio (isobutylthio) or 1,1-dimethylethylthio (tert-butylthio).

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The term "C₁-C₄-haloalkylthio" is a C₁-C₄-haloalkyl group, as defined above, attached via a sulfur atom. C₁-C₄-Haloalkylthio is, for example, SCH₂F, SCHF₂, SCF₃, SCH₂Cl, SCHCl₂, SCl₃, chlorofluoromethylthio, dichlorofluoromethylthio, chlorodifluoromethylthio, 2-fluoroethylthio, 2-chloroethylthio, 2-bromoethylthio, 2-iodoethylthio, 2,2-difluoroethylthio, 2,2,2-trifluoroethylthio, 2-

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chloro-2-fluoroethylthio, 2-chloro-2,2-difluoroethylthio, 2,2-dichloro-2-fluoroethylthio, 2,2,2-trichloroethylthio, SC_2F_5 , 2-fluoropropylthio, 3-fluoropropylthio, 2,2-difluoropropylthio, 2,3-difluoropropylthio, 2-chloropropylthio, 3-chloropropylthio, 2,3-dichloropropylthio, 2-bromopropylthio, 3-bromopropylthio, 3,3,3-trifluoropropylthio, 3,3,3-trichloropropylthio, $\text{SCH}_2\text{-C}_2\text{F}_5$, $\text{SCF}_2\text{-C}_2\text{F}_5$, 1-(CH_2F)-2-fluoroethylthio, 1-(CH_2Cl)-2-chloroethylthio, 1-(CH_2Br)-2-bromoethylthio, 4-fluorobutylthio, 4-chlorobutylthio, 4-bromobutylthio or nonafluorobutylthio.

The term " $\text{C}_1\text{-C}_4\text{-alkylsulfonyl}$ " is a $\text{C}_1\text{-C}_4\text{-alkyl}$ group, as defined above, attached via a sulfonyl [$\text{S}(\text{O})_2$] group. $\text{C}_1\text{-C}_4\text{-Alkylsulfonyl}$ is methylsulfonyl, ethylsulfonyl, n-propylsulfonyl, 1-methylethylsulfonyl (isopropylsulfonyl), n-butylsulfonyl, 1-methylpropylsulfonyl (sec-butylsulfonyl), 2-methylpropylsulfonyl (isobutylsulfonyl) or 1,1-dimethylethylsulfonyl (tert-butylsulfonyl).

The term " $\text{C}_1\text{-C}_4\text{-haloalkylsulfonyl}$ " is a $\text{C}_1\text{-C}_4\text{-haloalkyl}$ group, as defined above, attached via a sulfonyl [$\text{S}(\text{O})_2$] group. $\text{C}_1\text{-C}_4\text{-Haloalkylsulfonyl}$ is, for example, $\text{S}(\text{O})_2\text{CH}_2\text{F}$, $\text{S}(\text{O})_2\text{CHF}_2$, $\text{S}(\text{O})_2\text{CF}_3$, $\text{S}(\text{O})_2\text{CH}_2\text{Cl}$, $\text{S}(\text{O})_2\text{CHCl}_2$, $\text{S}(\text{O})_2\text{CCl}_3$, chlorofluoromethylsulfonyl, dichlorofluoromethylsulfonyl, chlorodifluoromethylsulfonyl, 2-fluoroethylsulfonyl, 2-chloroethylsulfonyl, 2-bromoethylsulfonyl, 2-iodoethylsulfonyl, 2,2-difluoroethylsulfonyl, 2,2,2-trifluoroethylsulfonyl, 2-chloro-2-fluoroethylsulfonyl, 2-chloro-2,2-difluoroethylsulfonyl, 2,2-dichloro-2-fluoroethylsulfonyl, 2,2,2-trichloroethylsulfonyl, $\text{S}(\text{O})_2\text{C}_2\text{F}_5$, 2-fluoropropylsulfonyl, 3-fluoropropylsulfonyl, 2,2-difluoropropylsulfonyl, 2,3-difluoropropylsulfonyl, 2-chloropropylsulfonyl, 3-chloropropylsulfonyl, 2,3-dichloropropylsulfonyl, 2-bromopropylsulfonyl, 3-bromopropylsulfonyl, 3,3,3-trifluoropropylsulfonyl, 3,3,3-trichloropropylsulfonyl, $\text{S}(\text{O})_2\text{CH}_2\text{-C}_2\text{F}_5$, $\text{S}(\text{O})_2\text{CF}_2\text{-C}_2\text{F}_5$, 1-(CH_2F)-2-fluoroethylsulfonyl, 1-(CH_2Cl)-2-chloroethylsulfonyl, 1-(CH_2Br)-2-bromoethylsulfonyl, 4-fluorobutylsulfonyl, 4-chlorobutylsulfonyl, 4-bromobutylsulfonyl or nonafluorobutylsulfonyl.

Carboxyl is $\text{-C}(\text{O})\text{OH}$.

The term " $\text{C}_1\text{-C}_4\text{-alkylcarbonyl}$ " denotes a $\text{C}_1\text{-C}_4\text{-alkyl}$ group, as defined above, attached via a carbonyl [$\text{C}(\text{=O})$] group. Examples are acetyl (methylcarbonyl), propionyl (ethylcarbonyl), propylcarbonyl, isopropylcarbonyl, n-butylcarbonyl and the like.

The term " $\text{C}_1\text{-C}_4\text{-haloalkylcarbonyl}$ " denotes a $\text{C}_1\text{-C}_4\text{-haloalkyl}$ group, as defined above, attached via a carbonyl [$\text{C}(\text{=O})$] group. Examples are trifluoromethylcarbonyl, 2,2,2-trifluoroethylcarbonyl and the like.

The term " $\text{C}_1\text{-C}_4\text{-alkoxycarbonyl}$ " denotes a $\text{C}_1\text{-C}_4\text{-alkoxy}$ group, as defined above, attached via a carbonyl [$\text{C}(\text{=O})$] group. Examples are methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, n-butoxycarbonyl and the like.

The term "C₁-C₄-haloalkoxycarbonyl" denotes a C₁-C₄-haloalkoxy group, as defined above, attached via a carbonyl [C(=O)] group. Examples are trifluoromethoxycarbonyl, 2,2,2-trifluoroethoxycarbonyl and the like.

- 5 The term "C₁-C₄-alkylcarbonyloxy" denotes a C₁-C₄-alkyl group, as defined above, attached via a carbonyloxy [C(=O)O] group. Examples are acetyloxy (methylcarbonyloxy), propionyloxy (ethylcarbonyloxy), propylcarbonyloxy, isopropylcarbonyloxy, n-butylcarbonyloxy and the like.

10 The term "C₁-C₄-haloalkylcarbonyloxy" denotes a C₁-C₄-haloalkyl group, as defined above, attached via a carbonyloxy [C(=O)O] group. Examples are trifluoromethylcarbonyloxy, 2,2,2-trifluoroethylcarbonyloxy and the like.

The term "C₁-C₄-alkylamino" is a group -N(H)C₁-C₄-alkyl. Examples are methylamino, ethylamino, propylamino, isopropylamino, butylamino and the like.

- 15 The term "di-(C₁-C₄-alkyl)amino" is a group -N(C₁-C₄-alkyl)₂. Examples are dimethylamino, diethylamino, ethylmethylamino, dipropylamino, diisopropylamino, methylpropylamino, methylisopropylamino, ethylpropylamino, ethylisopropylamino, dibutylamino and the like.

20 The term "C₁-C₄-alkylaminocarbonyl" is a group -C(O)-N(H)C₁-C₄-alkyl. Examples are methylaminocarbonyl, ethylaminocarbonyl, propylaminocarbonyl, isopropylaminocarbonyl, butylaminocarbonyl and the like.

25 The term "di-(C₁-C₄-alkyl)aminocarbonyl" is a group -C(O)-N(C₁-C₄-alkyl)₂. Examples are dimethylaminocarbonyl, diethylaminocarbonyl, ethylmethylaminocarbonyl, dipropylaminocarbonyl, diisopropylaminocarbonyl, methylpropylaminocarbonyl, methylisopropylaminocarbonyl, ethylpropylaminocarbonyl, ethylisopropylaminocarbonyl, dibutylaminocarbonyl and the like.

C₂-C₅-Alkylene is a linear or branched divalent alkyl radical having 2, 3, 4 or 5 carbon atoms. Examples are -CH₂CH₂-, -CH(CH₃)-, -CH₂CH₂CH₂-, -CH(CH₃)CH₂-,
 30 -CH₂CH(CH₃)-, -C(CH₃)₂-, -CH₂CH₂CH₂CH₂-, -CH(CH₃)CH₂CH₂-, -CH₂CH₂CH(CH₃)-,
 -C(CH₃)₂CH₂-, -CH₂C(CH₃)₂-, -CH₂CH₂CH₂CH₂CH₂-, -CH(CH₃)-CH₂-CH(CH₃)- and -CH₂-
 C(CH₃)₂-CH₂-.

C₂-C₆-Alkylene is a linear or branched divalent alkyl radical having 2, 3, 4, 5 or 6 carbon atoms.
 35 Examples, in addition to the radicals stated above for C₂-C₅-alkylene, are
 -CH₂CH₂CH₂CH₂CH₂CH₂-.

C₁-C₁₀-Alkylene is a linear or branched divalent alkyl radical having 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10
 40 carbon atoms. Examples, in addition to the radicals stated above for C₂-C₆-alkylene, are methylene (-CH₂-), -(CH₂)_n- with n = 7, 8, 9 or 10, and position isomers thereof.

Aryl is an aromatic carbocyclic ring. Examples are phenyl, naphthyl, phenanthrenyl and anthracenyl.

5 Aryl-C₁-C₄-alkyl is an aryl ring as defined above attached via a C₁-C₄-alkyl group as defined above. Examples are benzyl, 1-phenylethyl and phenethyl.

10 The composition containing semi-conducting single-walled carbon nanotubes generally contains at least one of the following carbonaceous materials: metallic single-walled carbon nanotubes, graphene, fullerenes, MWNTs, graphite, carbon black, amorphous carbon. Depending on the origin of the carbon source, the composition might also contain catalyst residues from the CNT production process which, of course, are to be unhitched as well. In particular, the composition containing semi-conducting single-walled carbon nanotubes also contains metallic single-walled carbon nanotubes, and optionally also graphene, fullerenes, MWNTs, graphite, carbon black and/or amorphous carbon.

15 In the method for separating semi-conducting single-walled carbon nanotubes from metallic single-walled carbon nanotubes, the composition of course contains both semi-conducting and metallic single-walled carbon nanotubes and optionally also other carbonaceous materials such as graphene, fullerenes, MWNTs, graphite, carbon black and/or amorphous carbon, and possibly also catalyst residues from the CNT production process.

25 The composition containing semi-conducting and metallic single-walled carbon nanotubes can be obtained by any of the known methods for producing CNTs, such as arc discharge, laser ablation, high-pressure carbon monoxide disproportionation (also termed high pressure CO conversion; HiPCO), plasma torch, aerosol synthesis, chemical vapor deposition (CVD) and combinations thereof. Most of these processes take place in a vacuum or with process gases. CVD growth of CNTs can occur in vacuum or at atmospheric pressure. Specifically, the composition is obtained by HiPCO. CNTs can be produced in the presence of catalysts, most commonly nickel, cobalt, iron or a combination thereof. The catalyst is generally provided in the form of metal nanoparticles. The catalyst may also be supported on an inert catalyst carrier, such as alumina or silica.

30 The obtained CNTs differ in various properties depending on the synthesis method; for example the diameters may range from 1.0 to 1.5 nm (synthesized by plasma torch), 0.7 to 1.2 nm (synthesized by HiPco) and 1.2 to 1.8 (synthesized by arc discharge).

40 Surface-active compounds are for example anionic, cationic, nonionic and amphoteric surfactants, block polymers, polyelectrolytes, and mixtures thereof. Examples of surfactants are listed in McCutcheon's, Vol.1: Emulsifiers & Detergents, McCutcheon's Directories, Glen Rock, USA, 2008 (International Ed. or North American Ed.).

Suitable anionic surfactants are for example alkali, alkaline earth or ammonium salts of sulfonates, sulfates, phosphates, carboxylates, and mixtures thereof. Examples of sulfonates are alkylarylsulfonates, diphenylsulfonates, alpha-olefin sulfonates, lignine sulfonates, sulfonates of fatty acids and oils, sulfonates of ethoxylated alkylphenols, sulfonates of alkoxyated arylphenols, sulfonates of condensed naphthalenes, sulfonates of dodecyl- and tridecylbenzenes, sulfonates of naphthalenes and alkylnaphthalenes, sulfosuccinates or sulfosuccinamates. Examples of sulfates are sulfates of fatty acids and oils, of ethoxylated alkylphenols, of alcohols, of ethoxylated alcohols, or of fatty acid esters. Examples of phosphates are phosphate esters. Examples of carboxylates are alkyl carboxylates, and carboxylated alcohol or alkylphenol ethoxylates.

Examples for nonionic surfactants are alkoxyates, N-substituted fatty acid amides, amine oxides, esters, sugar-based surfactants, polymeric surfactants, and mixtures thereof. Examples of alkoxyates are compounds such as alcohols, alkylphenols, amines, amides, arylphenols, fatty acids or fatty acid esters which have been alkoxyated with 1 to 50 equivalents. Ethylene oxide and/or propylene oxide may be employed for the alkoxyation, preferably ethylene oxide. Examples of N-substituted fatty acid amides are fatty acid glucamides or fatty acid alkanolamides. Examples of esters are fatty acid esters, glycerol esters or monoglycerides. Examples of sugar-based surfactants are sorbitans, ethoxylated sorbitans, sucrose and glucose esters or alkylpolyglucosides. Examples of polymeric surfactants are homo- or copolymers of vinylpyrrolidone, vinylalcohols, or vinylacetate.

Examples for cationic surfactants are quaternary surfactants, for example quaternary ammonium compounds with one or two hydrophobic groups, or salts of long-chain primary amines. Suitable amphoteric surfactants are alkylbetains and imidazolines. Suitable block polymers are block polymers of the A-B or A-B-A type comprising blocks of polyethylene oxide and polypropylene oxide, or of the A-B-C type comprising alkanol, polyethylene oxide and polypropylene oxide. Suitable polyelectrolytes are polyacids or polybases. Examples of polyacids are alkali salts of polyacrylic acid or polyacid comb polymers. Examples of polybases are polyvinylamines or polyethyleneamines.

The surface-active compound to be used in the present invention is preferably selected from polyarylethers, polyarylsulfonates, poly(alkyleneoxide) blockcopolymers, condensation products of at least one arylsulfonic acid, at least one aldehyde and optionally at least one further compound different from arylsulfonic acids and aldehydes which is capable of undergoing condensation with the arylsulfonic acid(s) and/or the aldehyde(s); and salts thereof.

Polyarylether surface-active compounds suitable for the present invention preferably contain an aryl backbone formed by 2 or more, preferably 5 to 100, more preferably 5 to 20 aryl moieties (e.g. benzene rings) bound to each other via suitable linking groups, such as alkylene groups, e.g. $(\text{CH}_2)_n$ with $n = 1$ to 4, $\text{CH}(\text{CH}_3)$, $\text{C}(\text{CH}_3)_2$, or $\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$; O, SO, SO_2 and the like. At

least a part of the aryl groups carry one or more ether groups, e.g. derived from alkylene oxides, such as ethylene oxide (EO), propylene oxide (PO), tetrahydrofuran or pentylene oxide. These are introduced, for example, by using aryl groups carrying one or more hydroxyl groups, which are reacted with EO, PO, tetrahydrofuran, pentylene oxide and/or the like, or with other compounds suitable for ether formation, such as hydroxyalkyl halides, tosylates or triflates, and the like. The ether groups are either terminated with -OH or can be partially or completely functionalized at this terminal -OH group and thus be converted, for example, into a sulfate (-O-S(=O)₂OR with R = hydrogen, C₁-C₄-alkyl or optionally substituted phenyl), sulfonate (-O-S(=O)₂-R' with R' = C₁-C₄-alkyl or phenyl), phosphate (-O-P(=O)(OR)₂ with each R being independently H, C₁-C₄-alkyl or optionally substituted phenyl), phosphonate (-O-P(=O)(R')OR with each R being independently H, C₁-C₄-alkyl or optionally substituted phenyl and R' being C₁-C₄-alkyl or phenyl), carboxylate (-O-C(=O)-R' with R' = hydrogen, C₁-C₄-alkyl or phenyl), carbonate (O-C(=O)-OR with R = hydrogen, C₁-C₄-alkyl or optionally substituted phenyl) or other functional group. Those functional groups which contain an OH group (i.e. which contain a radical R and in which R is H) may be partially or fully neutralized; i.e. by reaction with a base a part or all of the OH groups may be converted into OM groups wherein M is a metal cation equivalent (i.e. (M^{m+})_{1/m}, where m is the valence of the metal cation) or an ammonium cation (NR^aR^bR^cR^d)⁺, where R^a, R^b, R^c and R^d, independently of each other, are hydrogen, C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy (i.e. in this case R stands formally for a cation equivalent). The aryl groups may carry further radicals, for example radicals selected from alkyl, e.g. C₁-C₂₀-alkyl or long-chained alkyl groups derived from polyolefins with a number-average molecular weight of from 100 to 1000, e.g. alkyl groups derived from polyethylene, polypropylene, polybutylene and/or polyisobutylene; C₁-C₄-haloalkyl, halogen, hydroxyl, SH, SO₃H, OSO₃H, CN, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylthio, C₁-C₄-haloalkylthio, C₁-C₄-alkylsulfonyl, C₁-C₄-haloalkylsulfonyl, amino, C₁-C₄-alkylamino, di(C₁-C₄-alkyl)amino, carboxyl, C₁-C₄-alkylcarbonyl, C₁-C₄-haloalkylcarbonyl, C₁-C₄-alkoxycarbonyl, C₁-C₄-haloalkoxycarbonyl, C₁-C₄-alkylcarbonyloxy, C₁-C₄-haloalkylcarbonyloxy, aminocarbonyl, C₁-C₄-alkylaminocarbonyl, di(C₁-C₄-alkyl)aminocarbonyl, and the like. Also optionally present aryl groups which do not carry an ether groups may carry one or more of the above-listed further substituents.

Preferably, the aryl groups in the polyarylether surface-active compounds are phenyl or naphthyl rings, in particular phenyl rings, which may be substituted as defined above. Preferably, at least 50%, in particular at least 80% of the aryl groups carry one or more, e.g. 1 or 2, preferably 1, ether substituent as defined above or in the following. The ether substituents are preferably of formula -[O-A]_x-Y, wherein each A is independently selected from C₂-C₅-alkylene, each x is independently 1 to 100 and Y is selected from -OH, -O-S(=O)₂OR, -O-S(=O)₂-R', -O-P(=O)(OR)₂, -O-P(=O)(R')OR, -O-C(=O)-R' and -O-C(=O)-OR, where R and R' are as defined above. Preferably, A is selected from 1,2-ethylene and 1,2-propylene and is in particular 1,2-ethylene. Preferably, x is from 1 to 50. Preferably Y is selected from -OH, -O-S(=O)₂OR, -O-P(=O)(OR)₂ and -O-C(=O)-OR, where R is as defined above, and in particular from -OH and -O-P(=O)(OR)₂. Specifically, one part of the aryl rings

carry ether substituents in which Y is -OH and another part of the aryl rings carry ether substituents in which Y is -O-P(=O)(OR)₂. R is preferably H. R' is preferably C₁-C₄-alkyl.

Preferably the linking groups between the aryl rings are alkylene groups, especially CH₂.

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If the aryl groups or a part of the aryl groups carry further substituents, these are preferably selected from C₁-C₂₀-alkyl, halogen, hydroxyl, SO₃H, OSO₃H, CN and C₁-C₄-alkoxy.

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If present, aryl groups in the polyarylether surface-active compounds which do not carry an ether group as defined above are either unsubstituted (of course apart from their attachment points to the linking groups) or preferably carry 1, 2 or 3, preferably 1 or 2, of the above further substituents. Preferably, these substituents are selected from C₁-C₂₀-alkyl, halogen, hydroxyl, SO₃H, OSO₃H, CN and C₁-C₄-alkoxy, in particular from C₁-C₂₀-alkyl, hydroxyl and SO₃H, and in particular from C₄-C₂₀-alkyl and hydroxyl.

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Polyarylsulfonates as surface-active compounds suitable for the present invention preferably contain an aryl backbone formed by 2 or more, e.g. 5 to 100, aryl moieties (e.g. benzene or naphthalene rings) bound to each other via suitable linking groups, such as alkylene groups, e.g. (CH₂)_n with n = 1 to 4, CH(CH₃), C(CH₃)₂, or CH₂C(CH₃)₂CH₂; O, SO, SO₂, C(=O), C(=O)O, OC(=O)O and the like. At least a part of the aryl groups carry one or more sulfonate groups -S(=O)₂OR, wherein R is selected from hydrogen, a cationic equivalent, C₁-C₄-alkyl and phenyl. The sulfonate groups might be bound directly to the aryl groups or via a linking group, such as a C₁-C₁₀-alkylene group or a polyether group -[O-A]_x-, wherein A and x are as defined above. The sulfonic acid groups (i.e. the -S(=O)₂OR with R = H) may be partially or fully neutralized; i.e. by reaction with a base a part or all of the -S(=O)₂OH groups may be converted into -S(=O)₂OM groups wherein M is a metal cation equivalent (i.e. (M^{m+})_{1/m}, where m is the valence of the metal cation) or an ammonium cation (NR^aR^bR^cR^d)⁺, where R^a, R^b, R^c and R^d, independently of each other, are hydrogen, C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy (i.e. in this case R stands formally for a cation equivalent). Suitable bases are for example (M^{m+})(OH⁻)_m, (M^{m+})(CO₃⁻)_{m/2}, ammonia, an amine NR^aR^bR^c, etc., e.g. LiOH, NaOH, KOH, Na₂CO₃, K₂CO₃, NH₃, triethylamine, Hünig's base etc.

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Preferred polyarylsulfonates are the Glydol® brands from Zschimmer & Schwarz, especially Glydol® N1055.

Poly(alkyleneoxide) blockcopolymers are diblock, triblock or tetrablock copolymers or copolymers with a higher block number containing blocks of at least two different polymerized alkyleneoxides. In order to have amphiphilic properties, they contain at least one polyethyleneoxide (PEO) block. The other block(s) is/are preferably selected from polypropyleneoxide (PPO), poly(1,2-pentyleneoxide) block(s) and the like, and is/are in particular polypropyleneoxide block(s). Preference is given to triblock and tetrablock copolymers with polyethyleneoxide and polypropyleneoxide blocks, and especially to the copolymers of the Pluronic® and Tetronic®

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brands of BASF. Pluronics® are poloxamers. Poloxamers are nonionic triblock copolymers composed of a central hydrophobic chain of polyoxypropylene (polypropylene oxide; PPO) flanked by two hydrophilic chains of polyoxyethylene (polyethylene oxide; PEO). Particularly, the Pluronics® contain 10 to 100, preferably 15 to 70, in particular 20 to 60 PO repeating units in the central PPO block and on each side 10 to 150, preferably 20 to 100 EO repeating units in each PEO block. Tetronics® are X-shaped copolymers with four PPO-PEO blocks bonded to a central ethylene diamine linker.

In the condensation products of at least one arylsulfonic acid, at least one aldehyde and optionally at least one further compound different from arylsulfonic acids and aldehydes which is capable of undergoing condensation with the arylsulfonic acid(s) and/or the aldehyde(s) the arylsulfonic acid is preferably selected from naphthylsulfonic acid, phenylsulfonic acid and phenolsulfonic acid and in particular from 1- and especially 2-naphthylsulfonic acid and phenolsulfonic acid.

Suitable aldehydes are for example formaldehyde, acetaldehyde, propionaldehyde or butyraldehyde. The aldehyde is preferably formaldehyde.

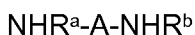
The further compound different from arylsulfonic acids and aldehydes is preferably selected from urea, urea derivatives, amines having at least two primary and/or secondary amino groups, melamine, melamine derivatives and hydroxyaromatic compounds, such as phenol, resorcinol, hydroquinone, catechol or the naphtholes.

The urea derivatives of components are for example

- substituted ureas of formula $R^1R^2N-C(=O)-NR^3R^4$, in which R^1 , R^2 , R^3 , and R^4 independently of one another are selected from hydrogen, C_1 - C_{10} -alkyl, aryl, and aryl- C_1 - C_4 -alkyl, with at least one of the radicals R^1 , R^2 , R^3 , and R^4 not being hydrogen; or R^1 and R^2 and/or R^3 and R^4 each together are C_2 - C_5 -alkylene, with one methylene group (i.e., a CH_2 group in the alkylene chain) optionally being replaced by a carbonyl group;
- or R^1 and R^3 together are C_2 - C_5 -alkylene, with one methylene group (i.e., a CH_2 group in the alkylene chain) optionally being replaced by a carbonyl group;
- or R^1 and R^2 and/or R^3 and R^4 , in each case together with the nitrogen atom to which they are attached, form a 5- or 6-membered unsaturated aromatic or nonaromatic ring which may comprise one or two further nitrogen atoms or a sulfur atom or oxygen atom as ring member (i.e., R^1 and R^2 , and/or R^3 and R^4 , together with the nitrogen atom to which they are attached, stand for a 5- or 6-membered unsaturated aromatic or nonaromatic ring which is attached via N and may comprise one or two further nitrogen atoms or one sulfur atom or oxygen atom as ring member);
- biuret

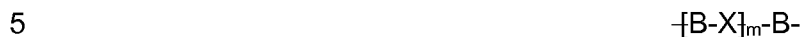
- thiourea;
- substituted thioureas of formula $R^5R^6N-C(=S)-NR^7R^8$, in which R^5 , R^6 , R^7 , and R^8 independently of one another are selected from hydrogen, C_1-C_{10} -alkyl, aryl, and aryl- C_1-C_4 -alkyl, with at least one of the radicals R^5 , R^6 , R^7 , and R^8 not being hydrogen;
 - 5 or R^5 and R^6 and/or R^7 and R^8 each together are C_2-C_5 -alkylene, with one methylene group (i.e., a CH_2 group in the alkylene chain) optionally being replaced by a carbonyl group;
 - or R^5 and R^7 together are C_2-C_5 -alkylene, with one methylene group (i.e., a CH_2 group in the alkylene chain) optionally being replaced by a carbonyl group;
 - 10 or R^5 and R^6 and/or R^7 and R^8 , in each case together with the nitrogen atom to which they are attached, form a 5- or 6-membered unsaturated aromatic or nonaromatic ring which may comprise one or two further nitrogen atoms or a sulfur atom or oxygen atom as ring member (i.e., R^5 and R^6 , and/or R^7 and R^8 , together with the nitrogen atom to which they are attached, stand for a 5- or 6-membered unsaturated aromatic or nonaromatic ring
 - 15 which is attached via N and may comprise one or two further nitrogen atoms or one sulfur atom or oxygen atom as ring member);
- guanidine;
 - substituted guanidines of the formula $R^9R^{10}N-C(=NR^{11})-NR^{12}R^{13}$, in which R^9 , R^{10} , R^{11} , R^{12} , and R^{13} independently of one another are selected from hydrogen, C_1-C_{10} -alkyl, aryl, and aryl- C_1-C_4 -alkyl, with at least one of the radicals R^9 , R^{10} , R^{11} , R^{12} , and R^{13} not being hydrogen; or R^9 and R^{10} and/or R^{12} and R^{13} each together are C_2-C_5 -alkylene, with one methylene group (i.e., a CH_2 group in the alkylene chain), optionally being replaced by a carbonyl group;
 - 20 or R^9 and R^{12} together are C_2-C_5 -alkylene, with one methylene group (i.e. a CH_2 group in the alkylene chain), optionally being replaced by a carbonyl group;
 - 25 or R^9 and R^{10} and/or R^{12} and R^{13} , in each case together with the nitrogen atom to which they are attached, form a 5- or 6-membered unsaturated aromatic or nonaromatic ring which may further comprise one further nitrogen atom, sulfur atom or oxygen atom as ring member (i.e., R^9 and R^{10} , and/or R^{12} and R^{13} , together with the nitrogen atom to which they are attached, stand for a 5- or 6-membered unsaturated aromatic or nonaromatic ring
 - 30 which is attached via N and may comprise one or two further nitrogen atoms or one sulfur atom or oxygen atom as ring member); or
 - carbonic esters of the formula $R^{14}-O-CO-O-R^{15}$, in which R^{14} and R^{15} independently of one another are selected from C_1-C_{10} -alkyl, aryl, and aryl- C_1-C_4 -alkyl, or R^{14} and R^{15} together are C_2-C_5 -alkylene.
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Amines having at least two primary and/or secondary amino groups are for example amines of the formula



40 in which

A is a divalent aliphatic, alicyclic, aliphatic-alicyclic, aromatic or araliphatic radical, with the aforementioned radicals also possibly being interrupted by a carbonyl group or by a sulfone group and/or possibly substituted by 1, 2, 3 or 4 radicals selected from C₁-C₄-alkyl; or is a divalent radical of the formula



in which

each X is independently O or NR^c, in which R^c is H, C₁-C₄-alkyl, C₂-C₄-hydroxyalkyl or C₁-C₄-alkoxy, and preferably is H, C₁-C₄-alkyl or C₁-C₄-alkoxy;

each B independently of one another is C₂-C₆-alkylene; and

10 m is a number from 1 to 100; preferably 1 to 80, and more particularly 1 to 20; and

R^a and R^b independently of one another are H, C₁-C₄-alkyl, C₂-C₄-hydroxyalkyl or C₁-C₄-alkoxy, and preferably are H, C₁-C₄-alkyl or C₁-C₄-alkoxy,

such as 1,2-ethylenediamine, 1,2- and 1,3-propylenediamine, 2,2-dimethyl-1,3-propanediamine, 15 1,4-butylenediamine, 1,5-pentylenediamine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, 2,2,4- or 2,4,4-trimethyl-1,6-hexamethylenediamine, 1,5-diamino-2-methylpentane, 1,4-diamino-4-methylpentan, 1,2-diaminocyclopentane, 1,3-diaminocyclopentane, 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, 1,4-diaminocyclohexane, 1-methyl-2,4-diaminocyclohexane, 1-methyl-2,6-diaminocyclohexane, diaminodicyclohexylmethane, isophoronediamine, 1,1-bis(aminomethyl)cyclohexane, 1,2-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)cyclohexane, 1,4-bis(aminomethyl)cyclohexane, 2-aminopropylcyclohexylamine, 3(4)-aminomethyl-1-methylcyclohexylamine, o-, m-, and p-phenylenediamine, o-, m-, and p-tolylenediamine, xylylenediamine, 1,2-, 1,3-, 1,4-, 1,5-, 1,8-, 2,3-, 2,6-, and 2,7-naphthylene, 2,2', 3,3', and 4,4'-diaminodiphenyl sulfone, 2,2', 25 3,3', and 4,4'-diaminobenzophenone, and 2,2', 3,3', and 4,4'-diaminodiphenylmethane, amine-terminated polyoxyalkylene polyols, examples being Jeffamines, such as 4,9-dioxadodecane-1,12-diamine and 4,7,10-trioxatridecane-1,13-diamine, or else more regular amine-terminated polyoxyalkylene polyols, such as amine-terminated polyethylene glycols, amine-terminated polypropylene glycols or amine-terminated polybutylene glycols, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethyleneheptamine, heptaethyleneoctamine, octaethylenenonamine, higher polyimines, bis(3-aminopropyl)amine, or bis(3-aminopropyl)methylamine.

Melamine derivatives are for example benzoguanamine, substituted melamines, and melamine 35 condensates, such as melam, melem, melon, and higher condensates. Melam (empirical formula C₆H₉N₁₁) is a dimeric condensation product of 2,4-diamino-6-chloro-s-triazine with melamine. Melem (empirical formula C₆H₆N₁₀) is the tri-amino-substituted tri-s-triazine (1,3,4,6,7,9,9b-heptaazaphenalene). Melon (empirical formula C₆H₃N₉) is likewise a heptazine.

40 The further compound different from arylsulfonic acids and aldehydes is in particular selected from urea and phenol.

The condensation products of at least one arylsulfonic acid, at least one aldehyde and optionally at least one further compound different from arylsulfonic acids and aldehydes which is capable of undergoing condensation with the arylsulfonic acid(s) and/or the aldehyde(s) the arylsulfonic acid is in particular a condensation product of naphthylsulfonic acid and formaldehyde, such as the Tamol® N brands from BASF, or a condensation product of phenolsulfonic acid, formaldehyde, urea and phenol, such as the Tamol® DN or PP brands from BASF.

In the above condensation products the sulfonic acid groups may be partially or fully neutralized; i.e. by reaction with a base a part or all of the $-S(=O)_2OH$ groups may be converted into $-S(=O)_2OM$ groups wherein M is a metal cation equivalent (i.e. $(M^{m+})_{1/m}$, where m is the valence of the metal cation) or an ammonium cation $(NR^aR^bR^cR^d)^+$, where R^a , R^b , R^c and R^d , independently of each other, are hydrogen, C_1 - C_{10} -alkyl or C_1 - C_{10} -alkoxy (i.e. in this case R stands formally for a cation equivalent). Suitable bases are for example $(M^{m+})(OH^-)_m$, $(M^{m+})(CO_3^{2-})_{m/2}$, ammonia, an amine $NR^aR^bR^c$, etc., e.g. LiOH, NaOH, KOH, Na_2CO_3 , K_2CO_3 , NH_3 , triethylamine, Hünig's base etc.

In case that semi-conducting single-walled carbon nanotubes are to be obtained, the surface-active compound is preferably selected from polyarylethers containing phosphate groups $-O-P(=O)(OR)_2$ and/or phosphonate groups $-O-P(=O)(R')OR$, where each R is independently selected from hydrogen, a cationic equivalent, C_1 - C_4 -alkyl and optionally substituted phenyl and R' is selected from C_1 - C_4 -alkyl and phenyl; and containing preferably phosphate groups $-O-P(=O)(OR)_2$.

If R is a cationic equivalent, the group $-OR$ is group $-OM$ wherein M is a metal cation equivalent (i.e. $(M^{m+})_{1/m}$, where m is the valence of the metal cation) or an ammonium cation $(NR^aR^bR^cR^d)^+$, where R^a , R^b , R^c and R^d , independently of each other, are hydrogen, C_1 - C_{10} -alkyl or C_1 - C_{10} -alkoxy. Such groups $-OM$ are generally obtained by partially or fully neutralizing polyarylethers containing one or more OH groups (i.e. containing a radical R and in which R is H); i.e. by reacting them with a base, such as $(M^{m+})(OH^-)_m$, $(M^{m+})(CO_3^{2-})_{m/2}$, ammonia, an amine $NR^aR^bR^c$, etc., e.g. LiOH, NaOH, KOH, Na_2CO_3 , K_2CO_3 , NH_3 , triethylamine, Hühig's base etc., so that a part or all of the OH groups are converted into OM groups.

More preferably, the surface-active compound is selected from polyarylethers having a backbone formed by 2 or more, preferably 5 to 100, more preferably 5 to 50 aryl moieties selected from phenyl and naphthyl rings bound to each other via linking groups selected from C_1 - C_5 -alkylene groups, preferably methylene (CH_2), where at least a part of the aryl groups, preferably at least 50%, in particular at least 80% of the aryl groups, carry one or more, preferably 1 or 2, in particular 1, ether groups of formula $-[O-A]_x-Y$, wherein each A is independently selected from C_2 - C_5 -alkylene, each x is independently 1 to 50, in a part of the ether groups Y is OH, in a part of the ether groups Y is $-O-P(=O)(OR)_2$, and, optionally, in a part of the ether groups Y may be selected from $-O-S(=O)_2OR$, $-O-S(=O)_2R'$, $-O-P(=O)(R')OR$, $-O-C(=O)-R'$ and $-O-C(=O)-OR$,

where each R is independently selected from hydrogen, C₁-C₄-alkyl and optionally substituted phenyl and each R' is independently selected from C₁-C₄-alkyl and phenyl, and where R can also stand for a cationic equivalent; and where preferably A is selected from 1,2-ethylene and 1,2-propylene, in particular 1,2-ethylene, Y is selected from -OH and -O-P(=O)(OR)₂, where one part of the aryl rings carry ether groups in which Y is -OH and another part of the aryl rings carry ether groups in which Y is -O-P(=O)(OR)₂, and where x is 5 to 50, preferably 10 to 40 if Y is OH, and x is 1 if Y is -O-P(=O)(OR)₂.

R is preferably H. R' is preferably C₁-C₄-alkyl.

If the aryl groups or a part of the aryl groups carry further substituents, these are preferably selected from C₁-C₂₀-alkyl, halogen, hydroxyl, SO₃H, OSO₃H, CN and C₁-C₄-alkoxy.

If present, aryl groups in the polyarylether surface-active compounds which do not carry an ether group as defined above are either unsubstituted (of course apart from their attachment points to the linking groups) or preferably carry 1, 2 or 3, preferably 1 or 2, of the above further substituents. Preferably, these substituents are selected from C₁-C₂₀-alkyl, halogen, hydroxyl, SO₃H, OSO₃H, CN and C₁-C₄-alkoxy, in particular from C₁-C₂₀-alkyl, hydroxyl and SO₃H, and in particular from C₄-C₂₀-alkyl and hydroxyl.

Preferably, the polyarylether is obtainable by the condensation of

- (1) at least one monohydroxyaromatic derivative in which the hydroxyl group is etherified with a C₂-C₅-alkyl group which carries a phosphate group -O-P(=O)(OR)₂, with each R being independently H, a cationic equivalent (definition see above), C₁-C₄-alkyl or optionally substituted phenyl;
 - (2) at least one monohydroxyaromatic derivative in which the hydroxyl group is etherified by reaction with at least one diol precursor selected from ethylene oxide, propylene oxide, tetrahydrofuran and 1,2-pentylene oxide;
 - (3) at least one monohydroxyaromatic compound carrying one or more C₁₀-C₂₀-alkyl groups; and
 - (4) an aldehyde source;
- and if desired partial or complete neutralization of the obtained product.

"Monohydroxyaromatic compound" refers to an aromatic compound carrying only one hydroxyl group (and optionally other substituents different from OH). The "monohydroxyaromatic derivative" in (1) and (2) is derived from such a monohydroxyaromatic compound. The monohydroxyaromatic compound in (3) or from which (1) and (2) derive is for example a hydroxybenzene or a hydroxynaphthalene, preferably a hydroxybenzene, where the phenyl or naphthyl ring, apart from the hydroxyl group (and the mandatory C₁₀-C₂₀-alkyl group(s) in (3)), may carry 1 or 2 further substituents such as C₁-C₄-alkyl, C₁-C₄-haloalkyl, cyano, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, and the like. Preferably, the phenyl or naphthyl rings do not carry any further substituents.

In (1) the C₂-C₅-alkyl group is preferably a C₂-C₃-alkyl group, more preferably a C₂-alkyl group.

In (2) the diol precursor is preferably selected from ethylene oxide and propylene oxide and is in particular ethylene oxide. The compound (2) contains preferably from 5 to 50, in particular from 10 to 40 repeating units of the diol precursor; i.e. is obtained by reacting 1 mole of hydroxyaromatic compound with 5 to 50, preferably 10 to 40 moles of diol precursor.

In (3) the monohydroxyaromatic compound carries preferably just one C₁₀-C₂₀-alkyl group. The alkyl group is preferably a C₁₀-C₁₆-alkyl group, and especially a C₁₂-alkyl group.

Suitable aldehydes (4) are for example formaldehyde, acetaldehyde, propionaldehyde or butyraldehyde or compounds from which these aldehydes are accessible (called aldehyde sources). Examples for formaldehyde sources are gaseous formaldehyde, formalin solutions, formaldehyde oligomers, such as trioxane or tetraoxane, and formaldehyde polymers, such as paraformaldehyde. Preference is given to formaldehyde, which, for practical reasons, is preferably used in form of trioxane or paraformaldehyde.

In particular, the polyarylether is obtainable by the condensation of

- (1) at least one monohydroxyaromatic derivative obtainable by the reaction (esterification) of phenoxyethanol and phosphoric acid or polyphosphoric acid;
 - (2) at least one monohydroxyaromatic derivative obtainable by the reaction [(poly)addition reaction] of phenol and ethylene oxide, preferably with 5 to 50, in particular 10 to 40 moles of ethylene oxide per mole of phenol;
 - (3) dodecylphenol; and
 - (4) a formaldehyde source;
- and if desired partial or complete neutralization of the obtained product.

Preferably, the at least one monohydroxyaromatic derivative (1) is used in molar excess to the overall amount of (2) and (3).

(2) and (3) are preferably used in a molar ratio of from 10:1 to 1:10, more preferably 5:1 to 1:5 and in particular from 2:1 to 1:2.

The aldehyde (4) is used in a sufficiently high amount to allow coupling of compounds (1), (2) and (3).

The condensation reaction is generally carried out in the presence of a catalyst. Suitable catalysts for such condensation reactions are known and are for example protic acids, such as sulfuric acid, phosphoric acid, sulfonic acids, such as methane sulfonic acid, trifluoromethane sulfonic acid or toluenesulfonic acid, and carboxylic acids, such as trifluoroacetic acid; or Lewis acids, such as aluminum trihalides, e.g. aluminum trichloride or tribromide, boron trihalides, such

as boron trifluoride or trichloride, or iron(III) halides, such as ferric chloride or bromide. Among these, preference is given to protic acids, especially to the above sulfonic acids.

5 The condensation reaction is generally carried out at elevated temperature, e.g. at from 60 to 180°C, preferably from 90 to 150°C.

If desired, after completion of the condensation the product can be neutralized, e.g. by addition of a base, e.g. of aqueous NaOH, KOH, Na₂CO₃ or the like.

10 The polyarylether has preferably a number average molecular weight M_n of from 1000 to 50000, more preferably from 3000 to 30000 and in particular from 5000 to 20000.

The polyarylether has preferably a dispersity (M_w/M_n ; M_w being the weight average molecular weight) of from 1 to 10, in particular from 1 to 5 and specifically from 1.1 to 2.

15 Solid sodium polytungstate (SPT), or sodium metatungstate (synonymous), $3\text{Na}_2\text{WO}_4 \cdot 9\text{WO}_3 \cdot \text{H}_2\text{O}$ or $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$, is a 12-fold aggregated isopolytungstate with a molar mass of 2986.12 g/mol. The structure of polytungstate is modelled using octahedra in which the oxygen atoms are located at the corners and the tungsten atoms at the center of the octahedra.
20 When represented as a spherical model, the oxygen atoms form a dense spherical shell while the tungsten atoms fill the open spaces in the octahedra. Because of this structure this substance may be considered a true metatungstate, represented structurally as $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$. In true metatungstates, both of the protons are located in the central empty space of the polyanion and are unable to penetrate the external shell of the spherical casing. Solid SPT has the form of
25 white crystals and aqueous SPT is a light yellow-green transparent solution. Due to its very high solubility in water (max. density 3.1 g/cm³), SPT is widely used as a heavy liquid for gravity separation (sink swim analysis) and density gradient centrifugation mainly used in the mineral industry (B. Plewinsky, R. Kamps, Makromol. Chem 1984, 185, 1429-1439; M.R. Gregory, K.A. Johnston, New Zealand Journal of Geology and Geophysics, 1987, 30, 317-320). Aqueous SPT
30 is non-toxic, non-flammable, non-corrosive, odorless, environmentally benign and reusable. Additionally it has a low viscosity, even at high concentrations.

The polytungstate is preferably one analogous to SPT (i.e. $M_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$, wherein M is a cation equivalent), wherein the counter cation (equivalent) is not restricted to sodium, but can be any
35 counter cation, provided that the corresponding polytungstate is soluble in aqueous media. Suitable counter cations are metal cation equivalents, i.e. $(M^{m+})_{1/m}$, wherein M is a metal and m is the valence of the metal; and ammonium cations $(\text{NR}^a\text{R}^b\text{R}^c\text{R}^d)^+$, where R^a, R^b, R^c and R^d, independently of each other, are hydrogen, C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy. Preferred metal cation equivalents are alkali metal cations, such as Li⁺, Na⁺ or
40 K⁺, and alkaline earth metal cation equivalents, such as $(\text{Mg}^{2+})_{1/2}$ or $(\text{Ca}^{2+})_{1/2}$; alkali metal cations being preferred. Aqueous media/solutions are defined below. Preferably, the cation equivalent

is selected from Li^+ (the polytungstate thus being lithium polytungstate), Na^+ (the polytungstate thus being sodium polytungstate), K^+ (the polytungstate thus being potassium polytungstate) or NH_4^+ (the polytungstate thus being ammonium polytungstate). In particular, however, the polytungstate is sodium polytungstate (SPT).

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The solution of the polytungstate is preferably aqueous. This means that the solvent is either water or a mixture of water and at least one water-miscible organic solvent. Suitable organic solvents are for example lower alkanols, such as methanol, ethanol, propanol or isopropanol, polyols, such as ethylene glycol, propylene glycol, diethylene glycol or triethylene glycol, cyclic ethers, such as tetrahydrofuran, 1,3- or 1,4-dioxane, amides, such as dimethylformamide, and dimethylsulfoxide. Among these, preference is given to the above alkanols. If the aqueous solution contains at least one water-soluble organic solvent, this is preferably present in an overall amount of at most 50% by weight, preferably at most 20% by weight and in particular at most 10% by weight, based on the total weight of water plus organic solvent. Preferably, the liquid solution contains water as solvent, and no organic solvent.

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The solution of the polytungstate preferably contains at least one surface-active compound. Preferred surface-active compounds are those mentioned above which are brought into contact with the composition containing semi-conducting and/or metallic single-walled carbon nanotubes and (optionally) undesired carbonaceous material. Preferably, the surface-active compounds brought into contact with the composition containing semi-conducting and/or metallic single-walled carbon nanotubes and (optionally) undesired carbonaceous material and the surface-active compounds contained in the solution of the polytungstate are the same.

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Preferably, the solution of the polytungstate preferably contains at least one surface-active compound in an amount of from 0.05 to 5% by weight, more preferably from 0.5 to 5 % by weight, and in particular from 1 to 3 % by weight, based on the total weight of the solution of the polytungstate.

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For obtaining preferentially semi-conducting single-walled carbon nanotubes, preferably, the solution of the polytungstate has at least one zone with a density which corresponds to the density of a complex formed by semi-conducting single-walled carbon nanotubes and the at least one surface-active compound. This is generally in the range of from 1.05 to 1.40 g/cm³, specifically from 1.10 to 1.30 g/cm³. Accordingly, the solution of the polytungstate has preferably at least one zone with a density of from 1.05 to 1.40 g/cm³, specifically of from 1.10 to 1.30 g/cm³.

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It has been found that the role of the polytungstate is not limited to that of a density medium. In fact, one aspect of the separation effect of the polytungstate is its pH in solution. Aqueous polytungstate solutions are acidic, the exact pH depending, of course, on the respective concentration (the higher the concentration, the lower the pH). It has been observed that even when using a single layer of polytungstate with a single density (i.e. not a density gradient; the density being

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in the range of the isopycnic point of the complex formed by semi-conducting or metallic SWNTs; i.e. from 1.05 to 1.3 g/cm³), semi-conducting and metallic SWNTs are nevertheless separated. Depending on the surface-active compounds used, the metallic SWNTs (as well as other undesired carbonaceous material) precipitate. Without wishing to be bound by theory, it is assumed that acidic polytungstate solutions affect the complex formed by metallic SWNTs (and other carbonaceous material) and surfactant(s) if these are those preferably used for obtaining semi-conducting SWNTs (e.g. the above-described polyarylethers), while the complex formed by semi-conducting SWNTs and surfactant(s) stays essentially unaffected. As a consequence, "naked" metallic SWNTs and/or the altered complex with surfactants and further undesired carbonaceous material, which have significantly higher densities than the complex formed by semi-conducting SWNTs and surfactant(s), precipitate, and this even without applying any density gradient centrifugation.

Thus, preferably, the solution of the polytungstate/surface-active compound has at least one zone with a pH of below 7, preferably of at most 6, more preferably with a pH from 1 to 6, even more preferably from 1.5 to 5.5, even more preferably from 1.5 to 3.5, even more preferably from 1.5 to 3.0 (and of course with the proviso that the pH is not neutralized by the composition containing the material to be separated).

In principle, it is not necessary to carry out centrifugation as ultracentrifugation; lower rotational velocities are also sufficient. Ultracentrifugation is of course nevertheless a suitable method.

Preferably, centrifugation is carried out with a mean acceleration of from 100 to 300000 x g, preferably of from 2000 to 50000 x g, in particular of from 5000 to 15000 x g.

The centrifugation time depends on various factors, such as acceleration, the components in the composition from which the semi-conducting SWCNTs are to be separated, the pH of the polytungstate solution etc. and may vary in wide ranges, such as from 0.5 to 30 h or 5 to 25 h or 10 to 20 h. The optimum time can be readily determined by preliminary tests. If the pH of the polytungstate solution is below 2, rather shorter centrifugation times are expedient because the polytungstate, especially SPT, may be prone to some degradation at very low pH values. If the temperature of the centrifugation is above 25 °C, rather shorter centrifugation times are expedient.

Preferably one or more layers of a solution of the polytungstate are placed in a centrifugation tube; whereas one layer is particular preferred. If two or more layers are used, these are placed on top each other. In case that two or more layers are used, the layers have different densities, so that they can form a density gradient, and are preferably placed in order of decreasing densities, the layer with the highest density being at the bottom of the centrifugation tube and the layer with the lowest density being at the top of the centrifugation tube.

If only one layer of the polytungstate solution is used, this has a density of preferably from 1.0 to 3.0 g/cm³, more preferably 1.0 to 2.0 g/cm³, even more preferably 1.0 to 1.5 g/cm³, even more preferably 1.0 to 1.4 g/cm³, even more preferably 1.05 to 1.3 g/cm³, specifically from 1.1 to 1.25 g/cm³.

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If two or more layers are used, one of these layers has a density of preferably from 1.0 to 3.0 g/cm³, more preferably 1.0 to 2.0 g/cm³, even more preferably 1.0 to 1.5 g/cm³, even more preferably 1.0 to 1.4 g/cm³, even more preferably 1.05 to 1.3 g/cm³, specifically from 1.1 to 1.2 g/cm³. Suitably, this layer is not the bottom layer, but the top or one of the middle layers.

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Preferably, if two or more layers of the solution of the polytungstate are used, the densities of the bottom layer and the top layer differ by at least 0.1 g/cm³, preferably by at least 0.2 g/cm³ and in particular by at least 0.5 g/cm³, e.g. by at least 0.7 g/cm³; the bottom layer suitably having the highest density and the top layer the lowest. Preferably the densities of the bottom layer and the top layer differ by 0.1 to 2.0 g/cm³, more preferably by 0.2 to 2.0 g/cm³, even more preferably by 0.5 to 2.0 g/cm³.

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The methods of the invention are preferably carried out as follows, comprising following steps:

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- (i) dispersing a composition containing semi-conducting and metallic single-walled carbon nanotubes and optionally other carbonaceous material or a composition containing semi-conducting single-walled carbon nanotubes and other carbonaceous material, in a liquid medium, preferably an aqueous medium, containing at least one surface-active compound to obtain a dispersion;
- (ii) providing a solution of a polytungstate;
- 25 (iii) placing the dispersion obtained in step (i) on or into the solution provided in step (ii);
- (iv) submitting the composition obtained in step (iii) to a centrifugation step, whereas the centrifugation is performed at a temperature of > 25°C;
- (v) separating the fraction or fractions enriched in semi-conducting single-walled carbon nanotubes from the fraction or fractions enriched in other carbonaceous material; in particular from the fraction or fractions enriched in metallic single-walled carbon nanotubes and from the fraction or fractions containing other carbonaceous material, if present;
- 30 (vi) if desired repeating steps (i) to (v) with one or more of the fractions obtained in step (v).

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The above remarks to preferred embodiments of the different aspects of the methods of the invention, such as to the composition containing semi-conducting and/or metallic SWCNTs, to the surface-active compound, to the polytungstate and the polytungstate solution, to specific forms of the density separation step etc. apply here, too.

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The liquid medium of step (i) is preferably aqueous, i.e. either water or a mixture of water and at least one water-soluble organic solvent. Suitable organic solvents are for example lower alka-

nols, such as methanol, ethanol, propanol or isopropanol, polyols, such as ethylene glycol, propylene glycol, diethylene glycol or triethylene glycol, cyclic ethers, such as tetrahydrofuran, 1,3- or 1,4-dioxane, amides, such as dimethylformamide and N-methylpyrrolidone, lower ketones, such as acetone and ethylmethylketone, and dimethylsulfoxide. Among these, preference is given to the above alkanols.

If the aqueous medium contains at least one water-soluble organic solvent, this is preferably present in an overall amount of at most 50% by weight, preferably at most 20% by weight and in particular at most 10% by weight, based on the total weight of water plus organic solvent.

Preferably, the liquid medium contains only water as solvent, and no organic solvent.

In step (i) the composition containing semi-conducting and/or metallic single-walled carbon nanotubes, calculated as solid carbon matter, is preferably used in an amount of from 0.001 to 2 % by weight, more preferable from 0.01 to 2 % by weight, in particular from 0.1 to 1 % by weight, based on the total weight of the dispersion; i.e. the dispersion obtained in step (i) contains the composition containing semi-conducting and/or metallic single-walled carbon nanotubes, calculated as solid carbon matter, in an amount of from 0.01 to 2 % by weight, in particular from 0.1 to 1 % by weight, based on the total weight of the dispersion.

The at least one surface-active compound is used in step (i) in an amount of from 0.05 to 5% by weight, more preferably of from 0.5 to 5 % by weight, in particular of from 1 to 3 % by weight, based on the total weight of the dispersion; i.e. the dispersion obtained in step (i) contains the at least one surface-active compound in an amount of from 0.05 to 5% by weight, in particular from 1 to 5 % by weight, based on the total weight of the dispersion.

Dispersion of the composition containing semi-conducting and/or metallic single-walled carbon nanotubes and (optionally) other carbonaceous material can be carried out by any means which ensures a fine and even distribution of the material in the dispersion, such as ultrasonic treatment (ultrasonic horn, ultrasonic bath, tip sonication and the like) or effective mechanical stirring or agitation, e.g. with an Ultra-Turrax® (from IKA®-Werke GmbH & Co. KG, Germany) or a Dispermat® (from Getzmann, Germany). Both pulsed or continuous treatments may be applied. Ultrasonic treatment is preferred.

Preferably, step (i) comprises providing a mixture containing semi-conducting and/or metallic single-walled carbon nanotubes and (optionally) other carbonaceous material, water and at least one surface-active compound and subjecting the mixture to an ultrasonic treatment.

Preferably, the temperature of the CNT dispersion, containing semi-conducting and metallic single-walled carbon nanotubes and/or optionally other carbonaceous material and at least one surface-active, during its preparation in step (i) is below 60°C, more preferably below 40°C,

more preferably below 30°C. For example the preparation of step (i) is carried out in an ice-cooled water bath.

5 Preferably, the pH of the CNT dispersion, containing semi-conducting and metallic single-walled carbon nanotubes and/or optionally other carbonaceous material and at least one surface-active, prepared in step (i) is below 7, more preferably below 6, even more preferably the pH is in the range from 2 to 5, even more preferably in the range from 3 to 4.

10 In step (ii), preferably one or more layers of a solution of the polytungstate are placed in a centrifugation tube. More preferable one layer of the polytungstate is placed in a centrifugation tube. If the density separation step (iv) is to be density gradient centrifugation, preferably two or more layers of a solution of the polytungstate are placed on top each other. In the latter case, i.e. in case that two or more layers are used, the layers have different densities and are preferably placed in order of decreasing densities, the layer with the highest density being at the bot-
15 tom of the centrifugation tube and the layer with the lowest density being at the top of the centrifugation tube. The densities of the bottom layer and the top layer differ preferably by at least 0.1 g/cm³, more preferably by at least 0.2 g/cm³ and in particular by at least 0.5 g/cm³, e.g. by at least 0.7 g/cm³.

20 In step (iii) the dispersion obtained in step (i) is placed on or into the solution provided in step (ii). This is done by usual means, such as overlaying the solution of step (ii) with the dispersion of step (i), e.g. with a (micro)pipette or a (micro)syringe or the like. If the dispersion of step (i) is placed "into" the solution provided in step (ii), this is usually done by first overlaying at least a part of the solution of step (ii) with the dispersion of step (i) and then overlaying the latter with
25 the remainder of the solution of step (ii) or just with water optionally containing surface-active compounds or with the solvent used for preparing the solution of step (ii). If the density separation step is sedimentation, placing the dispersion of step (i) "into" the solution provided in step (ii) can be carried out by simply mixing dispersion and solution.

30 In step (iv), the centrifugation is performed at a temperature of > 20°C; preferably of at least 22°C, more preferably of at least 25°C, preferably of > 25°C, more preferably of at least 28°C, more preferably of at least 30°C. Preferably the centrifugation is performed in a temperature range from >20 to 60°C, more preferably from at least 25 to 60°C, more preferably from > 25 to 60°C, more preferably from 22 to 50°C, more preferably from at least 25 to 50°C, more prefera-
35 bly from > 25 to 50°C, more preferably from 30 to 50°C, even more preferably from 22 to 45°C, even more preferably from 25 to 45°C, even more preferably from >25 to 45°C, even more preferably from 30 to 45°C, even more preferably from 25 to 40°C, even more preferably from >25 to 40°C, in particular from 30 to 40°C.

In step (v) the fraction or fractions enriched in semi-conducting single-walled carbon nanotubes is/are separated from the fraction or fractions enriched in other carbonaceous material. Convenient measures depend on the density separation step (iv) applied. For instance, density gradient centrifugation usually yields visible bands having a different optical aspect which can be separated by carefully removing the single layers, e.g. with a (micro)pipette or (micro)syringe or a piston gradient fractionator or another suitable means. This process can also be automatized. If centrifugation is carried out at a pH of below 5, preferably below 4, in particular below 3 and the surface-active compound is the one preferably used for obtaining semi-conducting single-walled carbon nanotubes, generally the fraction enriched in semi-conducting single-walled carbon nanotubes is found in the region with a density of from 1.05 to 1.3 g/cm³, while the other carbonaceous materials are found at the bottom of the centrifugation tube. This makes separation of the fraction enriched in semi-conducting single-walled carbon nanotubes much easier than in the density gradient ultracentrifugation methods of the prior art.

If desired the fraction(s) enriched in semi-conducting single-walled carbon nanotubes obtained in step (v) or other fractions can be resubmitted to steps (i) to (iv) in order to enhance purity and/or yield of the desired material, especially the semi-conducting SWCNTs.

For this purpose the fraction(s) to be resubmitted to steps (i) to (iv) are preferably first freed from solvent, polytungstate and surfactant. For instance, the fraction(s) containing the semi-conducting SWCNTs are diluted with water and centrifuged. The semi-conducting SWCNTs concentrate at the bottom in solid form. Thus the supernatant is discarded, the solid is washed with water which optionally contains surfactant and redispersed in analogy to step (i). All or selected steps may be repeated multiple times.

These steps can also be carried out to purify and isolate the desired semi-conducting SWCNTs without reintroducing them into steps (i) to (iv).

The polytungstate removed from the process may be purified and reused.

The whole process can also be carried out in a semi-continuous or continuous manner.

Moreover, the invention relates to semi-conducting single-walled carbon nanotubes, obtainable by the method of the invention. The semi-conducting single-walled carbon nanotubes of the invention have a particularly high purity. Preferably they have a purity of at least 95% by weight, more preferably of at least 98% by weight, even more preferably of at least 99% by weight, even more preferably of at least 99.2% by weight, in particular of at least 99.5% by weight. Preferably they contain less than 1% by weight, more preferably less than 0.9% by weight and in particular less than 0.8% by weight of metallic single-walled carbon nanotubes.

The invention also relates to the use of semi-conducting single-walled carbon nanotubes of the invention in electronic devices, optical devices, optoelectronic devices or energy storage devices; in particular in transistors, especially FETs and TFTs (for example for the use in back planes), memory devices, sensors, photodetectors, or solar cells.

5 The semi-conducting single-walled carbon nanotubes of the invention are in particular used in transistors; in particular in field-effect transistors (FETs), especially in FETs made from individual CNTs (see Park, H. et al.; Nature Nanotechnology 2012, 7,787–791) and in FETs made from CNT networks (Lau, P. H. et al.; Nano Lett. 2013, 13, 3864-3869). To these, great potential
10 for development is ascribed, for example in organic electronic devices such as back planes for display devices as well as storage elements and integrated optoelectronic devices. A further important application is in optical devices; especially in light-emitting diodes. Organic light-emitting diodes (OLEDs) are especially of interest as an alternative to cathode ray tubes and liquid-crystal displays for producing flat visual display units. Owing to the very compact design and the
15 intrinsically low power consumption, devices which comprise OLEDs are suitable especially for mobile applications, for example for applications in cell phones, laptops, etc. The semi-conducting single-walled carbon nanotubes of the invention are furthermore suitable for the use in memory devices, sensors (e. g. chemical sensors, temperature sensors, pressure sensors), photodetectors, solar cells and thin-film transistors (TFTs). The semi-conducting single-walled
20 carbon nanotubes of the invention may be applied for example via spin-coating, slot-die coating, screen printing, inkjet printing, flexographic printing, gravure printing, doctor blading, spray coating, drawdown-bar coating, aerosol deposition and the like. It is also possible to place the semi-conducting single-walled carbon nanotubes of the invention on specific positions on a functionalized substrate via ion-exchange techniques as described in Park, H. et al.; Nature Nanotechnology 2012, 7,787–791. By this approach, arrays of individually positioned semi-conducting
25 single-walled carbon nanotubes can be obtained.

Field-effect transistors generally comprise a substrate having at least one gate structure, a source electrode and a drain electrode as well as an insulating layer and at least one semiconductor material; in the present case semiconducting SWCNTs.
30

The semi-conducting SWCNTs can be in principle used as n-type semiconductors or as p-type semiconductors. Whether they act as n-type semiconductor or as p-type semiconductors depends inter alia on the employed transistor (contact materials, surface) and the measuring conditions (vacuum, air).
35

The semi-conducting SWCNTs of the invention may be used, for example, for the production of integrated circuits (ICs), for which customary n-channel MOSFETs (metal oxide semiconductor field-effect transistors) have been used to date. These are then CMOS-like semiconductor units,
40 for example for microprocessors, microcontrollers, static RAM and other digital logic circuits.

They are especially suitable for use in displays (specifically large-surface area and/or flexible displays), RFID tags, smart labels and sensors.

The optical device is for example an electroluminescent arrangement. Electroluminescent ar-
rangements generally comprise an upper electrode, a lower electrode, wherein at least one of
said electrodes is transparent, an electroluminescent layer and optionally an auxiliary layer,
wherein the electroluminescent arrangement comprises at least one semiconductor material; in
the present case semi-conducting SWCNTs. Preferably the electroluminescent arrangement is
in form of an organic light-emitting diode (OLED).

The invention is now further illustrated by the following examples.

Examples

1. Preparation of polyarylether surfactant PAE

The PAE was prepared according to the following phosphorylation and polycondensation procedure:

A reactor, equipped with heating and stirrer was charged with 127 g of polyphosphoric acid (specified to have 85 % P_2O_5 content). The content was heated to 90°C. 138.2 g (1 mol) of phenoxyethanol was added to the stirred reaction mixture through a period of 1 hour. After the addition was finished, the reaction mix was stirred for an additional hour. The reaction product contained 75 %-wt. of phenoxyethanol phosphoric acid monoester (ester of 1 mol of phenoxyethanol with 1 mol of phosphoric acid), 5 %-wt. of bis(phenoxyethanol)phosphoric acid ester (ester of 2 mols phenoxyethanol with 1 mol of phosphoric acid), 1 %-wt. of unreacted phenoxyethanol and 19 %-wt. of unreacted phosphoric acid. The reaction product of the phosphorylation was used without further purification as starting material for the following polycondensation step.

General polycondensation procedure:

A corrosion-resistant reactor equipped with a stirrer and temperature control was charged with the starting materials listed in table 1 in the given order:

1. poly(ethylenoxide)monophenylether (Ph-PEG), 2. phosphorylated phenoxyethanol (PPE), 3. dodecylphenol, 4. paraformaldehyde, 5. methansulfonic acid 98 %.

Upon completion of the addition of the acid, the reaction mix was heated to 95-100°C. After 2 hours the polycondensation reaction was finished and water was added. The polycondensate PAE was neutralized with NaOH to pH 7. Finally, the solid content of the product was adjusted with water to 36 %.

Table 1

Product	Ph-PEG		PPE ¹⁾	Dodecyl-phenol	Paraformaldehyde	CH ₃ SO ₃ H 98%	M _w ²⁾ Reaction product
	M _w [D]	[g]	[g]	[g]	[g]	[g]	[D]
PAE	1500	60.7	87.2	20.4	16.3	2.4	8000

¹⁾ contains 75 %-wt. of phenoxyethanol phosphoric acid monoester, 5 %-wt. of bis(phenoxyethanol)phosphoric acid ester, 1 %-wt. of phenoxyethanol and 19 %-wt. of phosphoric acid.

5 ²⁾ The molecular weights of the polymers were determined by using gel permeation chromatography method (GPC) as described below:

Column combination: OH-Pak SB-G, OH-Pak SB 804 HQ and OH-Pak SB 802.5 HQ by Shodex, Japan; eluent: 80 Vol.-% aqueous solution of HCO₂NH₄ (0.05 mol/l) and 20 Vol.-% acetonitrile; injection volume 100 µl; flow rate 0.5 ml/min. The molecular weight calibration was performed with poly(styrene sulphonate) standards for the UV detector and poly(ethylene oxide) standards for the RI detector. Both standards were purchased from PSS Polymer Standards Service, Germany. In order to determine the molecular weight of the polymers, result based on UV-detection (254 nm) was used, because the UV detector is only responsive towards the aromatic compounds and neglects inorganic impurities, that otherwise could falsify the results for the molecular weights.

2. Separation examples: centrifugation step at different temperatures

20 2a) Separation of HiPco SWCNTs

Preparation of SWCNT-dispersions: HiPco SWCNTs were purchased from NanoIntegris (Batch# HS 28030). The as-produced SWCNTs were dispersed in an aqueous solution containing 2 wt% of PAE by horn sonication for 1 h at 100% amplitude (Dr. Hielscher UP200s) starting with 0.5 wt% of raw nanotube material in a total of 50 g of dispersion. During sonication the vials were placed in ice-cooled water bath. The pH of the dispersion was adjusted to pH 4 by adding aliquots of 1M HCl.

Centrifugation process: For centrifugation, a water based solution of sodium polytungstate (SPT) (TC Tungsten Compounds) 25.5 wt% also containing 2 wt% of PAE was prepared. The pH-value of this SPT column was controlled by adding small aliquots of 1M HCl. The centrifugation vessel was loaded with 4.2 ml of SPT (pH 2.0) and 0.3 ml of the nanotube dispersion (pH 4) on top. Centrifugation (Beckman Coulter Optima XL) was performed applying a centrifugal field of approximately 10,000 x g for 18 h to separate nanotubes in a Beckman Coulter SW 60Ti rotor.

Temperature dependent centrifugation: The centrifugation conditions were kept as described above. After inserting the rotor into the centrifuge, the temperature was adjusted by an Peltier element and was allowed to settle for 0.5 - 4 h until equilibrium was reached ($\pm 0.1^\circ\text{C}$). The centrifugation was done at 10, 15, 25, 30 and 35°C .

5 Characterization of the separated SWCNTs: The extracted SWCNT fractions that still contained SPT and the PAE polymer were pelletized by centrifugation at $40.000 \times g$ for 17 h after dilution with DI-water. The supernatant was removed and the pellet was swirled up by refilling the centrifugation vessel with DI-water. This manoeuvre was repeated 2 times. Afterwards the pellet
10 was collected in an aqueous solution of 1 wt% of Sodium deoxycholate (Alfa-Aesar) (pH 7.2). Tip-sonication for 15 min was used to redisperse the SWCNTs. Optical analysis was performed by recording the absorbance spectra of post-treated samples with the Perkin Elmer UV-vis-NIR Spectrometer Lambda 250 with 1 cm cuvettes.

15

Temperature ($^\circ\text{C}$)	M11 / S22 Area ratio	relative purity indicator
10	0.79	0.72
15	0.81	0.70
20	0.77	0.74
25	0.68	0.84
30	0.57	1
35	0.57	1

Table 1. Summarizing the temperature dependent semiconducting purity. For the tested temperatures the purity of the SWCNT fractions was evaluated by integration of the S22 and M11 peak areas (without background subtraction). The calculated areas were used to form the
20 $A(\text{M11})/A(\text{S22})$ ratio. The smaller this ratio is the higher is the semiconducting purity of the extracted fractions at pH 2.0. The M11/S22 area ratio is inversely proportional to the semiconducting purity. The relative comparison of the determined ratios can therefore be used to further classify the semiconducting purity in dependence on the centrifugation temperature. The relative ratio comparison was defined as relative purity indicator varying with 1 being the highest purity
25 and 0.70 being the lowest purity.

2b) Separation of Arc Discharge SWCNTs

Preparation of SWCNT-dispersions: Arc Discharge SWCNTs were purchased from Carbon Solutions (Batch# P2). The as-produced SWCNTs were dispersed in an aqueous solution containing 2 wt% of PAE by horn sonication for 1 h at 100% amplitude (Dr. Hielscher UP200s) starting with 0.03 wt% of raw nanotube material in a total of 50 g of dispersion. During sonication the vials were placed in ice-cooled water bath. The pH of the dispersion was adjusted to pH 4 by adding aliquots of 1M HCl.

Centrifugation process: For centrifugation, a water based solution of sodium polytungstate (SPT) (TC Tungsten Compounds) 25.5 wt% also containing 2 wt% of PAE was prepared. The pH-value of this SPT column was controlled by adding small aliquots of 1M HCl. The centrifugation vessel was loaded with 3.8 ml of SPT (pH 4.3) and 0.7 ml of the nanotube dispersion (pH 4) on top. Centrifugation (Beckman Coulter Optima XL) was performed applying a centrifugal field of approximately 10,000 x g for 25 h to separate nanotubes in a Beckman Coulter SW 60Ti rotor.

Temperature dependent centrifugation: The centrifugation conditions were kept as described above. After inserting the rotor into the centrifuge, the temperature was adjusted by an Peltier element and was allowed to settle for 0.5 - 4 h until thermal equilibrium was reached ($\pm 0.1^\circ\text{C}$). The centrifugation was done at 10 and 30 °C.

Characterization of the separated SWCNTs: The extracted SWCNT fractions that still contained SPT and the PAE polymer were pelletized by centrifugation at 40.000 x g for 18 h after dilution with DI-water. The supernatant was removed. Afterwards the pellet was collected in an aqueous solution of 1 wt% of Sodium deoxycholate (Alfa-Aesar) (pH 7.2). Tip-sonication for 15 min was used to redisperse the SWCNTs. Optical analysis was performed by recording the absorbance spectra of post-treated samples with the Perkin Elmer UV-vis-NIR Spectrometer Lambda 250 with 1 cm cuvettes.

Temperature (°C)	M11 / S22 Area ratio	relative purity indicator
10	0.79	0.72
30	0.57	1

Table 1. Summarizing the temperature dependent semiconducting purity. For the tested temperatures the purity of the SWCNT fractions was evaluated by integration of the S22 and M11 peak areas (without background subtraction). The calculated areas were used to form the $A(\text{M11})/A(\text{S22})$ ratio. The smaller this ratio is the higher is the semiconducting purity of the ex-

5 tracted fractions at pH 4.3. The M11/S22 area ratio is inversely proportional to the semiconducting purity. The relative comparison of the determined ratios can therefore be used to further classify the semiconducting purity in dependence on the centrifugation temperature. The relative ratio comparison was defined as relative purity indicator varying with 1 being the highest purity and 0.72 being the lowest purity.

2c) Conclusion

The examples showed that centrifugation step performed at $> 25\text{ }^{\circ}\text{C}$ leads to higher semiconducting purity of CNTs.

Claims

1. Method for separating semi-conducting single-walled carbon nanotubes from metallic single-walled carbon nanotubes and, if present, from other carbonaceous material, or for separating semi-conducting single-walled carbon nanotubes from other carbonaceous material, whereas method comprises bringing a composition containing semi-conducting and metallic single-walled carbon nanotubes and optionally other carbonaceous material, or a composition containing semi-conducting carbon nanotubes and other carbonaceous material, into contact with at least one surface-active compound and with a solution of a polytungstate, and subjecting the obtained composition to a centrifugation step, whereas the centrifugation is performed at a temperature of $> 25^{\circ}\text{C}$ and whereas the surface-active compound is selected from polyarylethers, polyarylsulfonates, poly(alkyleneoxide) blockcopolymers, condensation products of at least one arylsulfonic acid, at least one aldehyde and optionally at least one further compound different from arylsulfonic acids and aldehydes which is capable of undergoing condensation with the arylsulfonic acid(s) and/or the aldehyde(s); and salts thereof.
2. The method as claimed in claim 1, comprising following steps:
- (i) dispersing a composition containing semi-conducting and metallic single-walled carbon nanotubes and optionally other carbonaceous material or a composition containing semi-conducting single-walled carbon nanotubes and other carbonaceous material, in a liquid medium, containing at least one surface-active compound to obtain a dispersion;
 - (ii) providing a solution of a polytungstate;
 - (iii) placing the dispersion obtained in step (i) on or into the solution provided in step (ii);
 - (iv) submitting the composition obtained in step (iii) to a centrifugation step, whereas the centrifugation is performed at a temperature of $> 25^{\circ}\text{C}$;
 - (v) separating the fraction or fractions enriched in semi-conducting single-walled carbon nanotubes from the fraction or fractions enriched in other carbonaceous material;
 - (vi) if desired repeating steps (i) to (v) with one or more of the fractions obtained in step (v).
3. The method as claimed in any of the preceding claims, where the centrifugation is performed at a temperature from > 25 to 60°C .
4. The method as claimed in any of the preceding claims, where the centrifugation is performed at a temperature of at least 30°C .

5. The method as claimed in any of the preceding claims, where the centrifugation is performed at a temperature from 30 to 60°C.
6. The method as claimed in any of the preceding claims, where the pH of the carbon nanotube dispersion prepared in step (i) is in the range from 2 to 5.
7. The method as claimed in any of the preceding claims, where the temperature of the carbon nanotube dispersion during its preparation in step (i) is below 40°C.
8. The method as claimed in any of the preceding claims, where the pH of the solution of a polytungstate is in the range from 1 to 6.
9. The method as claimed in any of the preceding claims, where the centrifugation is carried out with a mean acceleration of from 5000 to 15000 x g.
10. The method as claimed in any of the preceding claims, where in step (i) the composition containing single-walled carbon nanotubes, calculated as solid carbon matter, is used in an amount of from 0.01 to 2 % by weight, based on the total weight of the dispersion.
11. The method as claimed in any of the preceding claims, where in step (i) the liquid medium is an aqueous medium.
12. The method as claimed in any of the preceding claims, where in step (ii) the solution of a polytungstate is an aqueous solution.
13. The method as claimed in any of the preceding claims, where the polytungstate is sodium polytungstate.
14. The method as claimed in any of the preceding claims, where the surface-active compound is polyarylether.
15. Semi-conducting single-walled carbon nanotubes, obtained by a method as claimed in any claims 1 to 14.
16. The use of semi-conducting single-walled carbon nanotubes as defined in claim 15, in electronic devices, optical devices, optoelectronic devices or energy storage devices; in particular in transistors, memory devices, sensors, photodetectors, or solar cells.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/079989

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B32/172
ADD. H01L51/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2016/046153 A1 (BASF SE [DE]) 31 March 2016 (2016-03-31) cited in the application	15,16
A	abstract claims 1-32	1-14
A	----- HERSAM M C ET AL: "Sorting carbon nanotubes by electronic structure using density differentiation", NATURE NANOTECHNOLOGY, NATURE PUBLISHING GROUP, LONDON; GB, vol. 1, 4 October 2006 (2006-10-04), pages 60-66, XP002512670, DOI: 10.1038/NNANO.2006.52 abstract page 65, paragraph "centrifugation and fractionation" ----- -/--	1-16

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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- "&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/079989

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012/025150 A1 (HERSAM MARK C [US] ET AL) 2 February 2012 (2012-02-02) abstract examples 2,3a claim 1 -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

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