



(43) International Publication Date
28 August 2014 (28.08.2014)

(10) International Publication Number
WO 2014/127909 A1

(51) International Patent Classification:

H01B 1/00 (2006.01) *C08K 3/08* (2006.01)
C08L 65/00 (2006.01) *H01B 1/12* (2006.01)
C08L 25/18 (2006.01)

(21) International Application Number:

PCT/EP2014/000436

(22) International Filing Date:

18 February 2014 (18.02.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10 2013 002 855.8
20 February 2013 (20.02.2013) DE
61/769,374 26 February 2013 (26.02.2013) US

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: FORMULATIONS COMPRISING WASHED SILVER NANOWIRES AND PEDOT

(57) Abstract: The present invention relates to a process for the preparation of a composition which comprises a solvent A, silver nanowires and a conductive polymer, comprising the process steps: (i) the reduction of silver salts by means of a polyol serving as a solvent and reducing agent in the presence of a non-conductive polymer and subsequent precipitation of the silver nanowires thereby formed to obtain silver nanowires, on the surface of which at least some of the non-conductive polymer is adsorbed; (ii) the at least partial removal of the non-conductive polymer adsorbed on the surface of the silver nanowires to obtain purified silver nanowires; (iii) the bringing into contact of the purified silver nanowires with a solvent A and a conductive polymer. The present invention also relates to the compositions obtainable by this process, a composition which comprises a solvent, silver nanowires and a conductive polymer, a process for the production of an electrically conductive layer, the electrically conductive layer obtainable by this and the use of the compositions according to the invention.



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5 Formulations comprising washed silver nanowires and PEDOT

The present invention relates to a process for the preparation of a composition which comprises a solvent, silver nanowires and a conductive polymer, the composition obtainable by this process, a composition which comprises a solvent,
10 silver nanowires and a conductive polymer, a process for the production of an electrically conductive layer, the electrically conductive layer obtainable by this and the use of the compositions according to the invention.

Conductive polymers are increasingly gaining economic importance, since
15 polymers have advantages over metals with respect to processability, weight and targeted adjustment of properties by chemical modification. Examples of known π -conjugated polymers are polypyrroles, polythiophenes, polyanilines, polyacetylenes, polyphenylenes and poly(p-phenylene-vinylenes). Layers of conductive polymers are employed in diverse industrial uses, e.g. as polymeric
20 counter-electrodes in capacitors or for throughplating of electronic circuit boards. The preparation of conductive polymers is carried out chemically or electrochemically by oxidation from monomeric precursors, such as e.g. optionally substituted thiophenes, pyrroles and anilines and the particular optionally oligomeric derivatives thereof. In particular, chemically oxidative
25 polymerization is widely used, since it is easy to realize industrially in a liquid medium or on diverse substrates.

A particularly important polythiophene which is used industrially is poly(3,4-ethylenedioxythiophene) (PEDOT or PEDT), which is described, for example, in
30 EP 0 339 340 A2 and is prepared by chemical polymerization of 3,4-ethylenedioxythiophene (EDOT or EDT), and which has very high conductivities in its oxidized form. An overview of numerous poly(3,4-alkylenedioxythiophene)

derivatives, in particular poly(3,4-ethylenedioxythiophene) derivatives, and their monomer units, syntheses and uses is given by L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik & J. R. Reynolds, Adv. Mater. 12, (2000) p. 481–494. The dispersions, disclosed for example in EP 0 440 957 A2, of PEDOT with
5 polyanions, such as e.g. polystyrenesulphonic acid (PSS), have acquired particular industrial importance (PEDOT/PSS dispersions). Transparent, conductive films which have found a large number of uses, e.g. as a hole injection layer in organic light-emitting diodes (OLED) or as an intermediate layer in organic photovoltaic elements (OPV elements), can be produced from these dispersions. Due to the
10 polyelectrolyte properties of PEDOT as a polycation and PSS as a polyanion, the PEDOT/PSS compositions are not a true solution, but rather a dispersion. The extent to which polymers or parts of the polymers are dissolved or dispersed in this context depends on the weight ratio of the polycation and the polyanion, on the charge density of the polymers, on the salt concentration of the environment
15 and on the nature of the surrounding medium (V. Kabanov, Russian Chemical Reviews 74, 2005, 3–20). The transitions in this context can be fluid. No distinction is therefore made in the following between the terms "dispersed" and "dissolved". Similarly little distinction is made between "dispersing" and "dissolving" or between "dispersing agent" and "solvent". Rather, these terms are
20 used as being equivalent in the following.

OLED and OPV elements as a rule comprise a layer of indium tin oxide (ITO) as a conductive substrate layer. However, efforts are currently being made to dispense with the use of ITO, since in contrast to conductive polymer layers, for
25 example, this is not flexible. The disadvantage of the PEDOT/PSS-comprising dispersions known from the prior art is, however, that the conductivity of these layers is too low for them to be employed not only as a hole injection layer in an OLED or as an intermediate layer between the ITO-coated substrate and the semiconductor layer in the standard construction of a P3HT : PCBM solar cell,
30 but as a simultaneous substitute for the underlying ITO layer. So that layers comprising conductive polymers can replace the ITO layers in OLED and OPV

elements, they must have a particularly high conductivity (or a low surface resistance), with at the same time a high transmission.

Alternative materials which can be employed as an ITO substitute, such as, for
5 example, metal nanowires, are already known from the prior art. The production
of metal nanowires, and in particular the production of silver nanowires by the
polyol process are known (e.g. DE-A-10 2010 017706, US 7,585,349 or also WO-
A-2008/073143). A polyol serves here both as a solvent and as a reducing agent
10 for silver salts, preferably silver nitrate, a dispersing agent, such as
polyvinylpyrrolidone (PVP), and a halide source being available. The mixture of
the components is chosen such that a specific growth of the wires along a
preferred crystal axis develops. Anisotropic conductive bars having an aspect ratio
of at least 10 : 1 to 1,000 : 1 are formed by this means.

15 By application of these nanowires to a substrate, electrically conductive films of
low surface resistance (SR) and high conductivity and a transparency of > 80 %
can be achieved when the percolation threshold is exceeded. These can be applied
both to glass and especially to flexible substrates and show a constant
conductivity even after bending. By suitable structuring these transparent
20 electrodes can be used inter alia as an ITO substitute in electronic equipment, such
as LCD or plasma screens, touch screens and organic light-emitting diodes.

The silver nanowires can be applied in the form of dispersions, for example by
spin coating, spray coating or by "stamping on". However, if the silver nanowires
25 are processed from a dispersion without a film-forming agent, the silver
nanowires show only a poor adhesion to the surface and due to the loose bond
they are often only inadequately in contact and show relatively high surface
resistances. This makes it necessary to press the layers in order to increase the
conductivity, and/or to cover them with a further layer, for example a layer of a
30 TiO₂ sol/gel (Yang et al. ACS Nano 2011, 5, 9,877-9,882). Coatings with
conductive materials, in particular conductive polymers, are furthermore proposed
in the patent literature, as is described, for example in WO-A-2011/041232 or

WO-A-2008/131304. A stamping process in which the dry silver nanowires are applied to a prefabricated PEDOT/PSS layer is also known (Peumans et al. Adv. Mater. 2011, 23, 2905-2910).

- 5 The approaches described above for application of a conductive layer comprising silver nanowires to a substrate, however, are technically comparatively involved. However, a simple application of conductive layers by means of simple coating processes is desirable for use on an industrial scale. US-A-2012/0104374 describes the combining of a silver nanowire suspension with neutral to alkaline
- 10 PEDOT/PSS materials and uses these formulations for coating by spin coating. However, the application contains no indications of the quality of the silver nanowires employed which is necessary for the preparation of mixtures with conductive polymers. US-A-2012/0104374 gives no information on the purity of the silver nanowires employed there, in particular not on the amount of non-
- 15 conductive polymers which - due to the process for the production of silver nanowires - are conventionally adsorbed on the surface of the silver nanowires.

The present invention was based on the object of overcoming the disadvantages resulting from the prior art in connection with compositions comprising silver

20 nanowires, in particular in connection with the use of such compositions for the production of conductive layers which are suitable as an ITO substitute.

In particular, the present invention was based on the object of providing a composition comprising silver nanowires, from which electrically conductive

25 layers which are characterized by a low surface resistance with at the same time a high transmission and are therefore suitable as an ITO substitute material in an OLED, an OPV element or a touch screen can be produced in a simple manner on an industrial scale. In this context, the compositions should be distinguished in particular by a particularly advantageous storage stability.

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The present invention was furthermore based on the object of providing a process by means of which compositions which comprise silver nanowires and are advantageous in such a way can be prepared in a simple and reproducible manner.

5 A contribution towards achieving the abovementioned objects is made by a process for the preparation of a composition, preferably a dispersion, which comprises a solvent A, silver nanowires and a conductive polymer, comprising the process steps:

10 (i) the reduction of silver salts by means of a polyol serving as a solvent and reducing agent in the presence of a non-conductive polymer and subsequent precipitation of the silver nanowires formed thereby to obtain silver nanowires, on the surface of which at least some of the non-conductive polymer is adsorbed;

15

(ii) the at least partial removal of the non-conductive polymer adsorbed on the surface of the silver nanowires to obtain purified silver nanowires;

(iii) the bringing into contact of the purified silver nanowires with a solvent A
20 and a conductive polymer.

It has been found, surprisingly, that compositions which comprise electrically conductive polymers and have been prepared with silver nanowires which have first been purified by a washing process are distinguished in particular by a
25 significantly improved storage stability compared with compositions which have been prepared with non-washed silver nanowires.

In process step (i) of the process according to the invention, silver salts are first reduced by means of a polyol serving as a solvent and reducing agent in the
30 presence of a non-conductive polymer, and the silver nanowires formed by this procedure are then precipitated. This fundamental principle of the production of silver nanowires is adequately known from the prior art, for example from DE-A-

10 2010 017706. Process step (i) can accordingly include, for example, the part steps:

- 5 (ia) The provision of a reaction mixture comprising a polyol, a non-conductive polymer which adsorbs on to a silver surface, a chemical which forms a halide and/or one which forms a pseudohalide and a chemical which forms a redox pair, chosen from the group consisting of bromine, iodine, copper, vanadium and mixtures thereof;
- 10 (ib) the addition of a silver salt in an amount such that the concentration of silver in the reaction mixture is at least 0.5 wt.%, based on the total weight of the reaction mixture;
- (ic) the reduction of the silver salt at a temperature of the reaction mixture of at
15 least 75 °C for the duration of the reaction;
- (id) the separating off of the silver nanowires from the reaction mixture.

In this connection - just as in DE-A-10 2010 017706 - it should be pointed out that
20 the definition of the reaction mixture constituents "a chemical which forms a halide and/or one which forms a pseudohalide" and "a chemical which forms a redox pair, chosen from the group consisting of bromine, iodine, copper, vanadium and mixtures thereof" overlap. The chemicals bromine and iodine which form a redox pair are halogens which, in the form of one of their salts, are
25 both a "salt of a halide" and a "chemical which forms a redox pair, chosen from the group consisting of bromine and iodine".

Those compounds which are preferred as polyols, as non-conductive polymers which adsorb on to a silver surface (in DE-A-10 2010 017706 called "an organic
30 chemical which adsorbs on to a silver surface"), as a chemical which forms a halide and/or a pseudohalide, as a chemical which forms a redox pair, chosen from the group consisting of bromine, iodine, copper, vanadium and mixtures

thereof, and as a silver salt are the compounds which are already mentioned as preferred in DE-A-10 2010 017706.

Preferred polyols are accordingly chosen from the group consisting of 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, glycerol, trimethylolpropane, pentaerythritol, triethanolamine, trihydroxymethylaminomethane, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycols, dipropylene glycols and a polyethylene glycol which is liquid at the reaction temperature, such as, for example, polyethylene glycol 300. Very particularly preferred polyols are chosen from the group consisting of glycerol, ethylene glycol, tetraethylene glycol, 1,2-propanediol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol and 2,3-butanediol, the use of ethylene glycol and glycerol being most preferred.

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The non-conductive polymer which adsorbs on to the silver surface is required in the polyol process for formation of the desired wire-shaped morphology. In principle, all those compounds which are mentioned in WO-A-2009/128973 on pages 19 to 27 (paragraphs [0095] to [0116]) under the heading "Organic Protective Agent(s) (OPA)" can be employed as the non-conductive polymer. Preferred non-conductive polymers which adsorb on to a silver surface, however, are those having a weight-average molecular weight, preferably determined by gel permeation chromatography, of at least 100,000 g/mol, still more preferably at least 250,000 g/mol and most preferably at least 500,000 g/mol. In this connection, very particularly preferred non-conductive polymers are chosen from the group consisting of polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) and mixtures of various grades (molecular weights) and copolymers of these polymers. Suitable comonomers are e.g. N-vinylimidazole, vinyl acetate and vinylcaprolactam. However, the use of polyvinylpyrrolidone having a molecular weight of at least 100,000 g/mol, still more preferably at least 250,000 g/mol and most preferably at least 500,000 g/mol is most preferred as the non-conductive polymer.

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The chemical which forms a halide is preferably a salt of a halide, particularly preferably NaCl, NaBr, NaI, KCl, KBr, KI or a mixture of at least two of these, or elemental bromine, elemental iodine or a mixture of at least two of these, while
5 the chemical which forms the pseudohalide is preferably a salt of a pseudohalide, particularly preferably NaSCN, KSCN or a mixture of these.

The chemical which forms a redox pair is preferably elemental copper, elemental vanadium, a copper oxide, a vanadium oxide, a copper hydroxide, a vanadium
10 hydroxide, a copper sulphate, a vanadium sulphate, a copper nitrate, a vanadium nitrate, a vanadium trichloride or a mixture of these compounds. The chemical which forms a halide and the chemical which forms a redox pair are preferably already present in the reaction mixture provided in process step (ia). These chemicals (or at least one of these chemicals), however, can also be added only
15 subsequently, for example together with or after the addition of the silver salt in process step (ib).

With respect to the presence of possible further additives in the reaction mixture provided in process step (ia) and the relative amounts in which the particular
20 components are present in this mixture, reference is made to the teaching of DE-A-10 2010 017706, the disclosure content of which is a constituent of the disclosure of the present application with respect to the production of silver nanowires.

25 In process step (ib), a silver salt is then added in an amount such that the concentration of silver in the reaction mixture is at least 0.5 wt.%, based on the total weight of the reaction mixture, it being possible for the silver salt to be added, for example, at a temperature of the reaction mixture of at least 75 °C, particularly preferably at least 100 °C. AgNO₃ is preferred as the silver salt, and is
30 added to the reaction in the form of a solution or directly as a solid. A suitable solvent for the silver salt is, inter alia, the polyol employed in the reaction, that is to say preferably ethylene glycol and/or glycerol. The addition can take place all

at once, in portions or continuously over a relatively long period of time. The silver salt is added at the reaction temperature. The silver salt is added in an amount which corresponds mathematically to a silver concentration of at least 0.5 wt.% in the reaction mixture. In preferred embodiments of the process for the production of silver nanowires, silver is present in a concentration of at least 0.75 wt.%, more preferably of at least 1.0 wt.%, most preferably of at least 1.5 wt.%. 5

In process step (ic), the silver salt is then reduced, this reduction preferably being carried out at a temperature of at least 75 °C, particularly preferably of at least 100 °C and still more preferably of at least 120 °C for the duration of the reaction. As already described in DE-A-10 2010 017706, the formation of the silver nanowires can be readily monitored visually when carrying out this process. When the reaction has ended, the reaction mixture can be allowed to cool. A reaction mixture comprising silver nanowires, on the surface of which at least some of the non-conductive polymer is adsorbed, is obtained. The silver nanowires can then be separated off from this reaction mixture in a further part step (id), for example by precipitation after dilution of the reaction mixture by the addition of suitable solvents, such as, for example, acetone, tetrahydrofuran or ethyl acetate, or after addition of chemicals which modify the electrical double layer. The silver nanowires precipitated out in this manner can then be separated off from the liquid phase by processes known to the person skilled in the art, for example by centrifugation, filtration or by decanting. 10 15 20

Preferably, the silver nanowires are characterized by a length of from 1 µm to 200 µm, by a diameter of from 50 nm to 1,300 nm and by an aspect ratio (length : diameter) of at least 5 : 1, very particularly preferably by an aspect ratio in a range of from 10 : 1 to 1,000 : 1. 25

In process step (ii) of the process according to the invention, the non-conductive polymer adsorbed on the surface of the silver nanowires is at least partially removed to obtain purified silver nanowires. In particular, it is preferable in this 30

connection to remove in process step (ii) the non-conductive polymer adsorbed on the surface of the silver nanowires to an extent such that the weight ratio of silver : adsorbed non-conductive polymer is increased by a factor of at least 2, particularly preferably at least 5 and most preferably at least 10, starting from the weight ratio present after process step (i) has ended.

The at least partial removal of the non-conductive polymer adsorbed on the surface of the silver nanowires is preferably carried out by washing the silver nanowires obtained in process step (i) with a solvent B in which the non-conductive polymer is at least partly soluble. In this connection it has proved to be particularly advantageous if process step (ii) includes the following part steps:

(iia) the suspending of the silver nanowires obtained in process step (i) in a solvent B, in which the non-conductive polymer adsorbed on the surface of the silver nanowires is at least partly soluble;

(iib) the separating off of the suspended silver nanowires.

Possible solvents B which are employed in process step (iia) and in which the non-conductive polymer adsorbed on the surface of the silver nanowires is at least partly soluble are, if polyvinylpyrrolidone is used as the non-conductive polymer, in particular water, alcohols, such as methanol or ethanol, or mixtures of these. In this connection it is furthermore preferable for the silver nanowires to be suspended at a temperature in a range of from 15 to 100 °C, particularly preferably in a range of from 20 to 50 °C for a duration of from 1 minute to 5 hours, particularly preferably for a duration of from 5 minutes to 60 minutes. It is furthermore preferable for the silver nanowires to be suspended in an amount of from 1 g to 100 g, particularly preferably in an amount of from 2.5 g to 25 g of solvent B per gram of silver nanowires obtained in process step (i), preferably per gram of the composition obtained in process step (id) after the silver nanowires have been separated off.

The separating off of the suspended silver nanowires in process step (iib) is preferably again carried out by processes known to the person skilled in the art, particularly preferably by centrifugation.

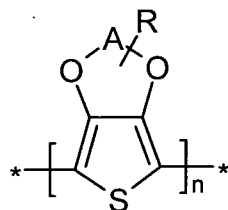
- 5 It has furthermore proved advantageous to purify the silver nanowires several times in succession, but particularly preferably twice, three times, four times or five times, by means of the washing process described by part steps (iia) and (iib), it having be found that the amount of non-conductive polymer adsorbed on the surface of the silver nanowires can be constantly reduced with an increasing
10 number of washing steps.

A continuous washing in which the silver nanowires obtained in process step (i) are brought into contact continuously with a solvent B in which the non-conductive polymer adsorbed on the surface of the silver nanowires is at least
15 partly soluble is also conceivable. This can be carried out, for example, by dialysis.

It is particularly preferable in this connection, if polyvinylpyrrolidone is used as the non-conductive polymer, for the nitrogen content of the purified silver
20 nanowires obtained in process step (ii) to be less than 7 wt.%, particularly preferably less than 2.5 wt.% and most preferably less than 1 wt.%, in each case based on the total weight of the drying residue of the purified silver nanowires.

In process step (iii) of the process according to the invention, the purified silver
25 nanowires are then brought into contact with a solvent A and a conductive polymer, but particularly preferably with a dispersion comprising a solvent A and a conductive polymer.

In this context, polythiophenes are particularly preferred as the conductive
30 polymer, in particular polythiophenes having the general formula



in which

5 A represents an optionally substituted C₁-C₅-alkylene radical,

10 R represents a linear or branched, optionally substituted C₁-C₁₈-alkyl radical, an optionally substituted C₅-C₁₂-cycloalkyl radical, an optionally substituted C₆-C₁₄-aryl radical, an optionally substituted C₇-C₁₈-aralkyl radical, an optionally substituted C₁-C₄-hydroxyalkyl radical or a hydroxyl radical, wherein 0 to 8 radicals R can be bonded to A and, in the case of more than one radical, can be identical or different.

The polythiophenes preferably in each case carry H on the end groups.

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In the context of the invention, C₁-C₅-alkylene radicals A are preferably methylene, ethylene, n-propylene, n-butylene or n-pentylene. C₁-C₁₈-alkyl R preferably represent linear or branched C₁-C₁₈-alkyl radicals, such as methyl, ethyl, n- or iso-propyl, n-, iso-, sec- or tert-butyl, n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl, C₅-C₁₂-cycloalkyl radicals R represent, for example, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl or cyclodecyl, C₅-C₁₄-aryl radicals R represent, for example, phenyl or naphthyl, and C₇-C₁₈-aralkyl radicals R represent, for example, benzyl, o-, m-, p-tolyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-xyllyl or mesityl. The preceding list serves to illustrate the invention by way of example and is not to be considered conclusive.

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In the context of the invention, numerous organic groups are possible as optionally further substituents of the radicals A and/or of the radicals R, for example alkyl, cycloalkyl, aryl, aralkyl, alkoxy, halogen, ether, thioether, disulphide, sulphoxide, sulphone, sulphonate, amino, aldehyde, keto, carboxylic acid ester, carboxylic acid, carbonate, carboxylate, cyano, alkylsilane and alkoxy silane groups and carboxamide groups.

Polythiophenes in which A represents an optionally substituted C₂-C₃-alkylene radical are particularly preferred. Poly(3,4-ethylenedioxythiophene) is very particularly preferred as the polythiophene.

The polythiophenes can be neutral or cationic. In preferred embodiments they are cationic, "cationic" relating only to the charges on the polythiophene main chain. The polythiophenes can carry positive and negative charges in the structural unit, depending on the substituent on the radicals R, the positive charges being on the polythiophene main chain and the negative charges optionally being on the radicals R substituted by sulphonate or carboxylate groups. In this context, the positive charges of the polythiophene main chain can be partly or completely satisfied by the anionic groups optionally present on the radicals R. Overall, in these cases the polythiophenes can be cationic, neutral or even anionic. Nevertheless, in the context of the invention they are all regarded as cationic polythiophenes, since the positive charges on the polythiophene main chain are the deciding factor. The positive charges are not shown in the formulae, since their precise number and position cannot be determined absolutely. However, the number of positive charges is at least 1 and at most n, where n is the total number of all recurring units (identical or different) within the polythiophene.

For compensation of the positive charge of the polythiophene, the conductive polymer furthermore comprises a polyanion which is preferably based on polymers functionalized with acid groups. Anions of polymeric carboxylic acids, such as polyacrylic acids, polymethacrylic acid or polymaleic acids, or of

polymeric sulphonic acids, such as polystyrenesulphonic acids and polyvinylsulphonic acids, are possible in particular as the polyanion. These polycarboxylic and -sulphonic acids can also be copolymers of vinylcarboxylic and vinylsulphonic acids with other polymerizable monomers, such as acrylic acid
5 esters and styrene. Polyanions which are furthermore possible are perfluorinated, colloid-forming polyanions, which are commercially obtainable, for example, under the name Nafion[®]. The molecular weight of the polymers which are functionalized with acid groups and supply the polyanions is preferably 1,000 to 2,000,000, particularly preferably 2,000 to 500,000. The polymers functionalized
10 with acid groups or their alkali metal salts are commercially obtainable, e.g. polystyrenesulphonic acids and polyacrylic acids, or can be prepared by known processes (see e.g. Houben Weyl, Methoden der organischen Chemie, vol. E 20 Makromolekulare Stoffe, part 2, (1987), p. 1141 et seq.).

15 Polymers functionalized with acid groups (polyanions) and polythiophenes, in particular polystyrenesulphonic acid and poly(3,4-ethylenedioxythiophene), can be present in the conductive polymer employed in process step (iii) in a weight ratio of from 0.5 : 1 to 50 : 1, preferably from 1 : 1 to 30 : 1, particularly preferably 2 : 1 to 20 : 1. The weight of the electrically conductive polymers here
20 corresponds to the weight of the monomers employed for the preparation of the conductive polymers, assuming that complete conversion takes place during the polymerization.

Preferably, the conductive polymer employed in process step (iii) comprises
25 complexes of a polythiophene and a polyanion, very particularly preferably PEDOT/PSS complexes. Such complexes are obtainable by polymerizing the thiophene monomers, preferably 3,4-ethylenedioxythiophene, oxidatively in aqueous solution in the presence of the polyanions, preferably the polystyrenesulphonic acid.

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Preferred solvents A are water, aliphatic alcohols, such as methanol, ethanol, i-propanol and n-butanol, aliphatic ketones, such as acetone and methyl ethyl

ketone, aliphatic carboxylic acid esters, such as ethyl acetate and butyl acetate, aromatic hydrocarbons, such as toluene and xylene, aliphatic hydrocarbons, such as hexane, heptane and cyclohexane, chlorohydrocarbons, such as methylene chloride and dichloroethane, aliphatic nitriles, such as acetonitrile, aliphatic
5 sulphoxides and sulphones, such as dimethylsulphoxide and sulpholane, aliphatic carboxylic acid amides, such as methylacetamide and dimethylformamide, or aliphatic and araliphatic ethers, such as diethyl ether and anisole, the use of water as solvent A being most preferred in particular in the case of PEDOT/PSS complexes as the conductive polymer. Water or mixtures of water with the
10 abovementioned organic solvents can furthermore also be used as solvent A.

According to a particularly preferred embodiment of the process according to the invention, the purified silver nanowires obtained in process step (ii) are mixed in process step (iii) with an aqueous dispersion comprising, as the conductive
15 polymer, complexes of a polythiophene and a polyanion, particularly preferably PEDOT/PSS complexes, and water as solvent A. PEDOT/PSS dispersions which are suitable for this are commercially obtainable, for example, under the trade name CleviosTM. The solids content of such dispersions is conventionally in a range of from 0.1 to 10 wt.%, particularly preferably in a range of from 1 to
20 5 wt.%. However, it is also conceivable to prepare the conductive polymer in the presence of the purified silver nanowires in that polymerizable precursors of the conductive polymer (e.g. 3,4-ethylenedioxythiophene in the case of poly(3,4-ethylenedioxythiophene) as the conductive polymer) are polymerized in the presence of the purified silver nanowires and in the presents of polyanions, such
25 as polystyrenesulphonic acid.

It is furthermore preferable according to the invention for the purified silver nanowires obtained in process step (ii) and the conductive polymer to be employed in process step (iii) in a relative amount such that the weight ratio of
30 silver : conductive polymer in the composition is in a range of from 10 : 1 to 1 : 10, particularly preferably in a range of from 5 : 1 to 1 : 5 and most preferably in a range of from 2 : 1 to 1 : 2. If the complexes described above of polythiophenes

and polyanions are employed as conductive polymer, the above relative amounts stated relate to the weight ratio of silver : total amount of polythiophenes and polyanions.

5 In addition to solvent A, the silver nanowires and the conductive polymer, the composition obtainable by the process according to the invention can optionally comprise further additives, such as, for example, additives which increase the conductivity, antioxidants, adhesion promoters, acids or bases for regulation of the pH, binders, crosslinking agents, surfactants or other additives known to the
10 person skilled in the art as additives for PEDOT/PSS dispersions. These additives can in principle be added to the purified silver nanowires employed in process step (iii), the dispersions employed in process step (iii) comprising a conductive polymer, or the mixture of these two components obtained in process step (iii).

15 Surfactant is understood as meaning amphiphilic substances which have a hydrophilic head group and a hydrophobic part. The hydrophilic group can be either ionic or nonionic in nature. Due the molecular structure and the tendency to accumulate at interfaces, this substance class lowers the interfacial tension and leads to improved wetting properties. Suitable surfactants are, in particular,
20 anionic surfactants, such as e.g. alkylbenzenesulphonic acids and salts, paraffinsulphonates, alcohol sulphonates, ether sulphonates, sulphosuccinates, phosphate esters, alkyl ether carboxylic acids or carboxylates, cationic surfactants, such as e.g. quaternary alkylammonium salts, nonionic surfactants, such as e.g. linear alcohol ethoxylates, oxo alcohol ethoxylates, alkylphenol ethoxylates or
25 alkyl polyglucosides.

Conductivity additives for polythiophenes which can be employed are polyalkylene glycols, in particular polyethylene glycols or polypropylene glycols, polyglycerols or mixtures of these, polyols, such as propylene glycol and ethylene
30 glycol, sulfoxides, such as dimethylsulphoxide, carboxylic acid amides, such as methylacetamide, dimethylacetamide, dimethylformamide, N-methylpyrrolidone, N-cyclohexylpyrrolidone, ionic liquids or sugars, such as sorbitol, the use of high-

boiling solvents, such as DMSO or ethylene glycol, being very particularly preferred. Additions of from 2 to 5 wt.% of these additives to an aqueous PEDOT/PSS dispersion lead to a significant increase in conductivity in the film formation.

5

Antioxidants are reagents which prevent the oxidative degradation of materials, which is often promoted by UV light. In the case of a use of polythiophenes as the conductive polymer, aromatic polyhydroxy compounds have proved suitable. Antioxidants which are particularly preferred according to the invention are gallic acid and the propyl esters of gallic acid, since they have an inhibiting effect in the conductive layers produced from the composition. Within a month, under the same storage conditions as the non-protected layer, the value can be kept below 60 $\Omega/\square$. The amount in which the gallic acid or the propyl esters of gallic acid are employed in the process according to the invention is preferably in a range of from 0.001 to 5 wt.%, particularly preferably in a range of from 0.005 to 1 wt.% and most preferably in a range of from 0.01 to 0.2 wt.%, in each case based on the total weight of the composition obtained by the process according to the invention.

Possible adhesion promoters are, in particular, organofunctional silanes and hydrolysates thereof, e.g. 3-glycidoxypropyltrialkoxysilane, 3-aminopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, vinyltrimethoxysilane or octyltriethoxysilane, while crosslinking agents which can be employed are melamine compounds, masked isocyanates, functional silanes - e.g. tetraethoxysilane, alkoxysilane hydrolysates, e.g. based on tetraethoxysilane, epoxysilanes, such as 3-glycidoxypropyltrialkoxysilane, epoxides or oxetanes.

Suitable binders are polyalkylene glycols, polyvinyl acetate, polycarbonate, polyvinyl butyrate, polyacrylic acid esters, polymethacrylic acid esters, polystyrene, polyacrylonitrile, polyvinyl chloride, polybutadiene, polyisoprene,

polyesters, silicones, and also pyrrole/acrylic acid ester, vinyl acetate/acrylic acid ester and ethylene/vinyl acetate copolymers which are soluble in organic solvents.

Preferred bases for regulation of the pH are, in addition to ammonia, alkali metal hydroxides and alkaline earth metal hydroxides, in particular amines, particularly
 5 preferably primary, secondary or tertiary amines in which the alkyl groups are chosen from the group consisting of methyl-, ethyl-, n-propyl- or iso-propyl-. An example of a suitable amine is dimethylaminoethanol.

10 It is furthermore preferable according to the invention to establish a pH in a range of from 2 to 7, very particularly preferably in a range of from 4 to 6 in the compositions.

A contribution towards achieving the abovementioned objects is also made by a
 15 composition, preferably a dispersion, comprising a solvent, silver nanowires and a conductive polymer, which is obtainable by the process according to the invention. Preferably, this composition is characterized in that if $SR_{t=0}$ is the surface resistance (in $[\Omega/\square]$) of an electrically conductive layer produced from the composition at time t_0 and $SR_{t=30 \text{ days}}$ is the surface resistance (in $[\Omega/\square]$) of an
 20 electrically conductive layer produced of the same composition at time $t_{30 \text{ days}}$ after 30 days storage in a closed vessel at 25 °C with exclusion of light, then:

$$SR_{t=0} / SR_{t=30 \text{ days}} \geq 0.75.$$

25 Particularly preferably, $SR_{t=0} / SR_{t=30 \text{ days}} \geq 0.9$, still more preferably ≥ 0.95 and most preferably ≥ 0.99 .

A contribution towards achieving the abovementioned objects is also made by a composition, preferably a dispersion, comprising a solvent A, silver nanowires
 30 and a conductive polymer, wherein, if $SR_{t=0}$ is the surface resistance (in $[\Omega/\square]$) of an electrically conductive layer produced from the composition n at time t_0 and

$SR_{t=30 \text{ days}}$ is the surface resistance (in $[\Omega/\square]$) of an electrically conductive layer produced of the same composition at time $t_{30 \text{ days}}$ after 30 days storage in a closed vessel at 25 °C with exclusion of light, then:

5
$$SR_{t=0} / SR_{t=30 \text{ days}} \geq 0.75.$$

Particularly preferably, $SR_{t=0} / SR_{t=30 \text{ days}} \geq 0.9$, still more preferably ≥ 0.95 and most preferably ≥ 0.99 .

10 Preferred solvents A, silver nanowires and conductive polymers in this context are those solvents A, silver nanowires and conductive polymers which have already been described above as preferred solvents A, silver nanowires and conductive polymer in connection with the process according to the invention. In addition to solvent A, the silver nanowires and the conductive polymers, the dispersion
15 according to the invention can also comprise further additives, those additives which have already been mentioned above as preferred additives in connection with the process according to the invention being preferred.

Preferably, the composition according to the invention, preferably the dispersion
20 according to the invention, like the composition obtainable by the process according to the invention, is distinguished in that less than 1.5 g, particularly preferably less than 1.0 g, still more preferably less than 0.85 g and most preferably less than 0.1 g of a non-conductive polymer per gram of silver are adsorbed on the surface of the silver nanowires in the composition. Those
25 polymers which have already been described above as preferred non-conductive polymers in connection with the process according to the invention are preferred as the non-conductive polymer in this context. It is accordingly particularly preferable according to the invention for less than 1.5 g, particularly preferably less than 1.0 g, still more preferably less than 0.85 g and most preferably less than
30 0.1 g of polyvinylpyrrolidone per gram of silver to be adsorbed on the surface of the silver nanowires in the composition.

In connection with the composition according to the invention, it is furthermore preferable for the nitrogen content, determined in the drying residue, of the silver nanowires in the composition to be less than 7 wt.%, particularly preferably less than 4 wt.% and most preferably less than 1 wt.%, in each case based on the total weight of the drying residue of the silver nanowires. The nitrogen content, determined in the drying residue of the total composition, is preferably less than 1 wt.% and particularly preferably less than 0.5 wt.%, in each case based on the total weight of the drying residue of the composition.

The composition according to the invention is furthermore preferably distinguished in that it comprises the silver nanowires and the conductive polymer in a relative amount such that the weight ratio of silver : conductive polymer in the dispersion is in a range of from 10 : 1 to 1 : 10, particularly preferably in a range of from 5 : 1 to 1 : 5 and most preferably in a range of from 2 : 1 to 1 : 2.

The pH of the dispersion according to the invention is preferably in a range of from 2 to 7, particularly preferably in a range of from 4 to 6.

A contribution towards achieving the abovementioned objects is also made by a process for the production of an electrically conductive layer, comprising the process steps:

- I) the provision of a substrate;
- II) the application of a composition obtainable by the process according to the invention or a composition according to the invention to the substrate;
- III) the at least partial removal of solvent A from the composition to obtain an electrically conductive layer on the substrate.

In process step I), a substrate is first provided, the nature of the substrate depending on the intended purpose for which the composition obtainable by the

process according to the invention or the composition according to the invention is employed. If the composition is employed, for example, for the production of a solid electrolyte layer in a capacitor, the substrate can be, for example, a porous anode body provided with a dielectric layer. If the dispersion is employed, for example, for the production of a hole injection layer in an OLED, the substrate can be, for example, a transparent electrode, such as ITO. Possible substrates are furthermore, in particular, films, particularly preferably polymer films, very particularly preferably polymer films of thermoplastic polymers, or glass plates.

10 In process step II), a composition obtainable by the process according to the invention or a composition according to the invention is then applied to the substrate, it being possible for this application to be carried out by known processes, e.g. by spin coating, impregnation, pouring, dripping on, spraying, misting, knife coating, brushing or printing, for example by ink-jet, screen, 15 gravure, offset or tampon printing, in a wet film thickness of from, for example, 0.5 μm to 250 μm , preferably in a wet film thickness of from 2 μm to 50 μm .

In process step III), at least some of solvent A is then removed from the composition to obtain an electrically conductive layer on the substrate, this removal preferably being carried out by a drying at a temperature in a range of 20 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$ of the substrate coated with the composition.

A contribution towards achieving the abovementioned objects is also made by an electrically conductive layer, which is obtainable by the process described above.

25

A contribution towards achieving the abovementioned objects is also made by the use of the composition obtainable by the process according to the invention or of the composition according to the invention for the production of an electrically conductive layer in an OLED, an OPV element, a touch screen, for shielding from electromagnetic radiation ("EMI shielding"), in sensors or for the production of an IR reflection layer. However, the use of the composition obtainable by the process according to the invention or of the composition according to the invention as an

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ITO substitute in an OLED, an OPV element or a touch screen is very particularly preferred.

The invention is now explained in more detail with the aid of test methods and
5 non-limiting examples.

Test methods

Determination of the surface resistance

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The surface resistance (SR) of the coatings is determined by means of the 4-point measurement method and stated in $\Omega/\square$.

Determination of the transmission

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The transmission of the coated substrates is determined on a 2-channel spectrometer (Lambda900, PerkinElmer). In order to rule out interferences of the scattered light here, the sample is measured in a photometer sphere (Ulbricht sphere), as a result of which scattered light and transmitted light are detected by
20 the photodetector. The transmission is thus understood as meaning 1-absorption of the coating and of the substrate.

The transmission of the pure substrate is first measured. Melinex 506 films having a thickness of 175 μm are used as the substrate. Thereafter, the coated substrate is
25 measured.

The transmission spectra are recorded in the range of visible light, i.e. from 320 nm to 780 nm with a step width of 5 nm.

30 The standard colour value Y of the sample is calculated from the spectra in accordance with DIN 5033, taking as the basis a 10° observer angle and light type D65. The internal transmission is calculated from the ratio of the standard colour

values of the substrate with coating (Y) to that without coating (Y_0): The internal transmission corresponds to $Y/Y_0 \times 100$ in per cent. For simplicity, only transmission is referred to the in the following.

5 Determination of the figure of merit

For better comparability of the results of the coatings, a figure of merit (FOM) of transmission and surface resistance is used, such as has been proposed by Gordon (R.G. Gordon, MRS Bulletin August 1996, page 52-57). This results from:

10

$$FOM = -\ln\left(\frac{Y}{Y_0}\right) \times SR$$

Determination of the haze

- 15 Haze values were determined with a Haze-gard plus from BYK Gardner (Geretsried).

CHN analysis

- 20 The drying residue for determination of the nitrogen content in the silver nanowires is obtained by drying 2 g of silver nanowires at 100 °C in vacuo (< 50 mbar) for 14 hours.

- 25 The determination of the element contents was performed at Currenta GmbH & Co. OHG as a commissioned analysis. The measurement was performed on a LECO TruSpec apparatus (LECO Corporation, St. Joseph, USA), and the carbon and hydrogen content are determined with an IR measurement cell. The nitrogen determination is carried out by means of a thermal conduction detector.

Examples

Example 1: Synthesis of silver nanowires (according to the invention)

5 Ethylene glycol (193 g, technical grade 98 %, Applichem Darmstadt) is initially introduced into a round-bottomed flask and heated, and polyvinylpyrrolidone (4.5 g, Luvitec K90, BASF, Ludwigshafen) is introduced while hot. A solution of silver nitrate (4.5 g, 63.5 % metal basis, Johnson Matthey, Enfield) in ethylene glycol (20.5 g) and a solution of vanadium chloride (9 mg, 99 %, Merck, 10 Darmstadt) in ethylene glycol (2.5 g) are then added and the mixture is heated to 120 °C. The longitudinal growth of the nanowires is monitored under the microscope and after conclusion of the growth the reaction is stopped by pouring the hot reaction mixture into a water bath. Mixture 1 is thereby obtained.

15 Example 2: Precipitation - silver nanowires (according to the invention)

130 ml of acetone are added to 50 g of mixture 1 from Example 1, while stirring. The start of sedimentation is indicated by the occurrence of larger aggregates. The mixture is left to rest for 30 min. The supernatant solution is discarded and 3.5 g 20 of a paste-like precipitate are obtained (mixture 2).

Example 3: Silver nanowires - 1st washing step (according to the invention)

5 g of the acetone-moist precipitate from Example 2 (mixture 2) are suspended in 25 20 g of water and the suspension is homogenized by shaking. The homogeneous mixture is centrifuged at 2,500 rpm for 20 min. The supernatant is removed and discarded and the sediment is topped up with water to 5 g and the mixture homogenized by shaking (mixture 3).

30 Example 4: Silver nanowires - 2nd washing step (according to the invention)

5 g of the suspension from Example 3 are suspended in 20 g of water and the suspension is homogenized by shaking. The homogeneous mixture is centrifuged at 2,500 rpm for 20 min. The supernatant is removed and discarded and the sediment is topped up with water to 5 g and the mixture homogenized by shaking (mixture 4).

Example 5: Silver nanowires - 3rd washing step (according to the invention)

5 g of the suspension from Example 4 are suspended in 20 g of water and the suspension is homogenized by shaking. The homogeneous mixture is centrifuged at 2,500 rpm for 20 min. The supernatant is removed and discarded and the sediment is topped up with water to 5 g and the mixture homogenized by shaking (mixture 5).

Example 6: CHN determination

In each case 2 g of the silver nanowire suspensions of mixtures 2 - 5 were dried at 100 °C in vacuo for 14 h. The constituents of the dry residue were determined by means of CHN analysis and the results are summarized in Table 1.

Table 1: CHN analysis and silver content (silver content calculated from gravimetry)

Element	Dry residue mixture 1	Dry residue mixture 2	Dry residue mixture 3	Dry residue mixture 4	Dry residue mixture 5
C	38.1	39.3	28.8	11.1	3.3
H	4.8	5.0	3.7	1.5	0.7
N	7.3	7.3	5.4	2.2	0.9
Ag	32.1	-	52.9	84	92.9

Table 1 clearly shows that by washing with water the content of nitrogen-containing component can be significantly reduced.

Example 7: Formulation of silver nanowires + Clevios PH 1000 (according to the invention)

0.83 g of mixture 3 from Example 3 (8.1 % Ag content gravimetrically, 67 mg of silver) were mixed with 7.64 g of water, 7.85 g of Clevios PH 1000 (86 mg of PEDOT/PSS, Heraeus Precious Metals, Leverkusen) and 0.755 g of dimethylsulphoxide (DMSO, ACS reagent, Sigma Aldrich, Munich). In the last step 50 µl of Triton X 100 (Sigma-Aldrich, Munich) are added to the formulation. The formulation was applied with spiral doctor blades from Erichsen (Erichsen K Hand Coater 620) to Melinex 506 films (Pütz GmbH + Co. Folien KG, Taunusstein), wet film thicknesses of 4, 6 and 12 µm thereby being realized. The coating was dried at 120 °C for 5 min. The measurement results of the coatings are summarized in Table 2.

Example 8: Formulation of silver nanowires washed twice - Clevios PH 1000 (according to the invention)

1.12 g of mixture 4 from Example 4 (6.0 % Ag content gravimetrically, 67 mg of silver) mixed with 7.35 g of water, 7.85 g of Clevios PH 1000 (86 mg of PEDOT/PSS) and 0.755 g of DMSO. In the last step 50 µl of Triton X 100 are added to the formulation. The formulation was applied with spiral doctor blades from Erichsen to Melinex 506 films, wet film thicknesses of 4, 6 and 12 µm thereby being realized. The coating was dried at 120 °C for 5 min. The measurement results of the coatings are summarized in Table 2.

25

Example 9: Formulation of silver nanowires washed 3 times - Clevios PH 1000 (according to the invention)

0.96 g of mixture 5 from Example 5 (7.0 % Ag content gravimetrically, 67 mg of silver) were mixed with 7.51 g of water, 7.85 g of Clevios PH 1000 (86 mg of PEDOT/PSS) and 0.755 g of DMSO. In the last step 50 µl of Triton X 100 are added to the formulation. The formulation was applied with spiral doctor blades

from Erichsen to Melinex 506 films, wet film thicknesses of 4, 6 and 12 μm thereby being realized. The coating was dried at 120 °C for 5 min. The measurement results of the coatings are summarized in Table 2.

- 5 Table 2: Coatings with formulations (silver nanowires content 0.4 %) - silver nanowires with various washing stages

Formulation	Washing steps	Wet film thickness [μm]	SR [$\Omega/\square$]	Transmission [%]	Haze [%]	FOM [Ω]
Example 7: Formulation of silver nanowires + Clevios PH 1000	1	4	1035	98.7	2.5	13.0
Example 8	2	4	443	98.8	1.7	5.2
Example 9	3	4	246	98.5	2.0	3.8
Example 7	1	6	435	97.0	3.8	13.0
Example 8	2	6	150	97.7	2.5	3.4
Example 9	3	6	63	97.2	3.1	1.8
Example 7	1	12	194	93.9	6.2	12.2
Example 8	2	12	51	94.9	4.3	2.7
Example 9	3	12	29	94.5	5.0	1.6

- Example 10: Formulation without high-boiling substance, 0.4 % of silver nanowires

2.48 g of mixture 5 from Example 5 (2.7 % Ag content gravimetrically, 67 mg of silver) were mixed with 7.51 g of water and 7.85 g of Clevios PH 1000 (86 mg of PEDOT/PSS). In the last step 50 μl of Triton X 100 are added to the formulation.

- 15 The formulation was applied with spiral doctor blades from Erichsen to Melinex 506 films, wet film thicknesses of 4, 6 and 12 μm thereby being realized. The coating was dried at 120 °C for 5 min. The measurement results of the coatings are summarized in Table 3.

Table 3: Formulation from Example 10 without conductivity additive, with 0.4 % silver nanowires content.

Formulation	Washing steps	Wet film thickness [μm]	SR [$\Omega/\square$]	Transmission [%]	Haze [%]	FOM [Ω]
Example 10	3	4	6613800	98.8	1.94	77433.3
Example 10	3	6	2664	97.6	3.07	64.4
Example 10	3	12	53	94.2	5.75	3.1

5 Example 11: Formulation without conductivity additive, 0.6 % of silver nanowires

3.70 g of mixture 5 from Example 5 (SAR 232-4)(2.7 % Ag content gravimetrically, 100 mg of silver) were mixed with 5.55 g of water and 7.85 g of Clevios PH 1000 (86 mg of PEDOT/PSS). In the last step 50 μl of Triton X 100
 10 are added to the formulation. The formulation was applied with spiral doctor blades from Erichsen to Melinex 506 films, wet film thicknesses of 4, 6 and 12 μm thereby being realized. The coating was dried at 120 °C for 5 min. The measurement results of the coatings are summarized in Table 4.

15 Table 4: Coatings on Melinex film 506 with formulation from Example 11, with 0.6 % silver nanowires content

Formulation	Washing steps	Wet film thickness [μm]	SR [$\Omega/\square$]	Transmission [%]	Haze [%]	FOM [Ω]
Example 11	3	4	2257752	98.5	2.39	33780
Example 11	3	6	126	97.2	4.28	3.6
Example 11	3	12	22	93.3	8.02	1.5

Example 12: Storage stability of the formulation from Example 9

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The formulation obtained in Example 9 was applied, after 30 days of storage, to Melinex 506 films using 6 μm spiral doctor blades from Erichsen. The coatings were dried at 120 °C for 5 min.

Table 5: Storage stability of Clevios - silver nanowire formulations.

Formulation	Wet film thickness [μm]	SR [$\Omega/\square$]	Transmission [%]	Haze [%]	FOM [Ω]
Example 9	6	63	97.2	3.1	1.8
Example 12	6	63	96.9	3.3	2.0

5 Example 13: Formulation from mixture 2 (0.6 % silver content)

0.999 g of mixture 2 from Example 2 (10 % Ag content gravimetrically, 100 mg of silver) was mixed with 7.5 g of water, 7.85 g of Clevios PH 1000 (86 mg of PEDOT/PSS) and 0.755 g of DMSO. In the last step 50 μl of Triton X 100 are
 10 added to the formulation. The formulation was applied with spiral doctor blades from Erichsen to Melinex 506 films, wet film thicknesses of 12 μm thereby being realized. The coating was dried at 120 °C for 5 min. The measurement results of the coatings are summarized in Table 6.

15 Example 14: Storage stability of the formulation from Example 13

The formulation obtained in Example 13 was applied, after 4 days of storage, to Melinex 506 films using a 12 μm spiral doctor blade from Erichsen. The coatings were dried at 120 °C for 5 min.

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Table 6: Storage stability of Clevios - silver nanowire formulations, non-washed silver nanowires

Formulation	Wet film thickness [μm]	SR [$\Omega/\square$]
Example 13	12	66.1
Example 14	12	142

Example 15: CHN analysis on dry residues of formulations.

5 g of the formulation from Example 9 were dried at 100 °C in a vacuum drying oven for 1 night and the sample was investigated by means of CHN analysis.

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Table 7: CHN analysis in Example 15.

Element	Example 9
C	38.3
H	4.3
N	0.3

Claims

- 5 1. A process for the preparation of a composition which comprises a solvent A, silver nanowires and a conductive polymer, comprising the process steps:
- 10 (i) the reduction of silver salts by means of a polyol serving as a solvent and reducing agent in the presence of a non-conductive polymer and subsequent precipitation of the silver nanowires thereby formed to obtain silver nanowires, on the surface of which at least some of the non-conductive polymer is adsorbed;
- 15 (ii) the at least partial removal of the non-conductive polymer adsorbed on the surface of the silver nanowires to obtain purified silver nanowires;
- (iii) the bringing into contact of the purified silver nanowires with a solvent A and a conductive polymer.
- 20 2. Process according to claim 1, wherein the non-conductive polymer employed in process step (i) has a weight-average molecular weight of at least 100,000 g/mol.
- 25 3. Process according to claim 1 or 2, wherein the non-conductive polymer is a polyvinylpyrrolidone.
- 30 4. Process according to one of the preceding claims, wherein the at least partial removal of the non-conductive polymer adsorbed on the surface of the silver nanowires is carried out in process step (ii) by washing the silver nanowires obtained in process step (i) with a solvent B in which the non-conductive polymer is at least partly soluble.

5. Process according to claim 3 and 4, wherein the solvent B used for the washing is water.
6. Process according to claim 3, wherein the nitrogen content of the purified silver nanowires obtained in process step (ii) is less than 7 wt.%, based on the total weight of the drying residue of the purified silver nanowires.
7. Process according to one of the preceding claims, wherein the conductive polymer employed in process step (iii) comprises a polythiophene.
8. Process according to claim 7, wherein the conductive polymer employed in process step (iii) comprises complexes of a polythiophene and a polyanion.
9. Process according to claim 8, wherein the conductive polymer employed in process step (iii) comprises PEDOT/PSS complexes.
10. Process according to one of the preceding claims, wherein in process step (iii) the purified silver nanowires obtained in process step (ii) are mixed with an aqueous composition comprising PEDOT/PSS complexes.
11. Process according to one of the preceding claims, wherein in process step (iii) the purified silver nanowires obtained in process step (ii) and the conductive polymer are employed in a relative amount such that the weight ratio of silver : conductive polymer in the composition is in a range of from 10 : 1 to 1 : 10.
12. A composition comprising a solvent A, silver nanowires and a conductive polymer, obtainable by the process according to one of claims 1 to 11.

13. Composition according to claim 12, wherein if $SR_{t=0}$ is the surface resistance (in $[\Omega/\square]$) of an electrically conductive layer produced from the composition at time t_0 and $SR_{t=30 \text{ days}}$ is the surface resistance (in $[\Omega/\square]$) of an electrically conductive layer produced of the same composition at time $t_{30 \text{ days}}$ after 30 days storage in a closed vessel at 25 °C with exclusion of light, then:

$$SR_{t=0} / SR_{t=30 \text{ days}} \geq 0.75.$$

14. A composition comprising a solvent A, silver nanowires and a conductive polymer, wherein, if $SR_{t=0}$ is the surface resistance (in $[\Omega/\square]$) of an electrically conductive layer produced from the composition at time t_0 and $SR_{t=30 \text{ days}}$ is the surface resistance (in $[\Omega/\square]$) of an electrically conductive layer produced of the same composition at time $t_{30 \text{ days}}$ after 30 days storage in a closed vessel at 25 °C with exclusion of light, then:

$$SR_{t=0} / SR_{t=30 \text{ days}} \geq 0.75.$$

15. Composition according to one of claims 12 to 14, wherein less than 1.5 g of a non-conductive polymer per gram of silver are adsorbed on the surface of the silver nanowires in the composition.

16. Composition according to one of claims 12 to 15, wherein the non-conductive polymer is polyvinylpyrrolidone.

17. Composition according to claim 16, wherein the nitrogen content of the composition determined in the drying residue is less than 1 wt.%, based on the total weight of the drying residue of the composition.

18. Composition according to one of claims 12 to 17, wherein the conductive polymer in the composition comprises a polythiophene.

19. Composition according to claim 18, wherein the conductive polymer in the composition comprises complexes of a polythiophene and a polyanion.
- 5 20. Composition according to claim 19, wherein the conductive polymer in the dispersion comprises PEDOT/PSS complexes.
21. Composition according to one of claims 12 to 20, wherein the composition comprises the silver nanowires and the conductive polymer
10 in a relative amount such that the weight ratio of silver : conductive polymer in the composition is in a range of from 10 : 1 to 1 : 10.
22. Composition according to one of claims 12 to 21, wherein the pH of the composition is in a range of from 2 to 7.
- 15 23. A process for the production of an electrically conductive layer, comprising the process steps:
I) the provision of a substrate;
II) the application of a composition according to one of claims 12 to
20 22 to the substrate;
III) the at least partial removal of solvent A from the composition to obtain an electrically conductive layer on the substrate.
24. An electrically conductive layer, obtainable by the process according to
25 claim 23.
25. Use of the composition according to one of claims 12 to 22 for the production of an electrically conductive layer in an OLED, an OPV element, a touch screen, for shielding from electromagnetic radiation
30 ("EMI shielding"), in sensors or for the production of an IR reflection layer.

26. Use of the composition according to one of claims 12 to 22 as an ITO substitute in an OLED, an OPV element or a touch screen.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/000436

A. CLASSIFICATION OF SUBJECT MATTER INV. H01B1/00 C08L65/00 C08L25/18 C08K3/08 H01B1/12 ADD.		
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) H01B C08L C08K		
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	US 2012/138913 A1 (ALSAYED AHMED [US] ET AL) 7 June 2012 (2012-06-07)	1-26
Y	page 10, paragraph 0156 - paragraph 0159 page 16, paragraph 0268 - paragraph 0271; examples 1-8 page 18 - page 20; claims 1-38	1-26
Y	US 2009/130433 A1 (TAKADA HIROSHI [JP]) 21 May 2009 (2009-05-21) page 8, paragraph 0119 - paragraph 0120 ----- -/-	1-26
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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 "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
30 July 2014		06/08/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Jung, Andreas

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/000436

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A	WHITNEY GAYNOR ET AL: "Smooth Nanowire/Polymer Composite Transparent Electrodes", ADVANCED MATERIALS, vol. 23, no. 26, 12 July 2011 (2011-07-12) , pages 2905-2910, XP055131272, ISSN: 0935-9648, DOI: 10.1002/adma.201100566 the whole document -----	1-26

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