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Composition comprising intrinsically conductive polymer

The invention relates to a composition comprising intrinsically conductive polymer, processes for its preparation and the use of this composition for the manufacture of electronic devices, and in particular the use as hole-injection layer in organic light-emitting diodes, so-called OLEDs.

Organic light-emitting diodes (OLEDs), in particular polymeric organic light-emitting diodes (sometimes also called PLEDs), are enjoying worldwide interest. From these the market is expecting novel high-performing displays, wherein a great future is predicted above all for PLEDs due to their simple manufacturing process by spin-coating or ink-jet printing and their simpler layer structure compared with OLEDs of low-molecular substances.

Usually an OLED consists of an anode, a so-called hole-injection layer, a layer with a light-emitting organic substance and a cathode of a metal with low work function such as Ca and Ba. Usually the OLEDs are encapsulated in order to prevent too rapid a decrease in performance.

Monochrome displays which can be prepared with PLEDs in adequate stability and brilliance, e.g. using the product "Super Yellow" of Covion GmbH, Frankfurt, are not adequately accepted in the market. However, such displays allow to observe differences in the quality of the hole-injection layer which is formed from conductive polymers. This layer is necessary because, at just about -4.3 eV, the indium tin oxide (ITO) customarily used as anode, does not alone provide a suitable level of work function and also, in operation, very quickly causes black dots and burnout of OLEDs and PLEDs.

Here, PEDOT doped with polystyrene sulphonic acid (PSSH) (Baytron P from H. C. Starck, Germany) has been established as the standard material because this raises the work function on the anodes to the desired level of -5.0 to 5.1 eV. In combination with the luminescent material "Super Yellow" a more than adequate stability of such light-emitting diodes is achieved. PEDOT/PSSH layers are usually applied from aqueous dispersion, e.g. by means of spin-coating or ink-jet printing. However, attempts to achieve this also with polyaniline which was likewise doped with PSSH failed.

Even if hole-injection layers which have been formed from polyaniline, namely PANI/PSSH, at roughly -5.1 eV, in principle exhibit the same work function as PEDOT/PSSH, in "pulsed operation" they display an inadequate stability and in some cases fail already after only 0.5 hours. During pulsed operation a higher voltage is applied than in direct-current operation, but only for a short time. On the other hand

PEDOT/PSSH permits continuous operation over several hundred of hours at increased temperature. An explanation for such different behaviour of PANI compared with PEDOT has thus far not been found.

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So far, however, neither material has been able to help improve the stability, necessary for colour displays ("RGB"), of the red, green and particularly the blue light-emitting polymers. Even with OLEDs made from low-molecular substances,
10 above all the blue light-emitting substances are the stability-limiting factor.

It is therefore the aim of numerous research groups and industrial enterprises, on the one hand to overcome the
15 intrinsic instability above all of the blue light-emitters but also, on the other, to develop novel hole-injection materials which likewise help increase stability.

Currently two approaches, or a combination thereof, to the
20 solution of the problem are preferred:

1. Increasing the amount of the work function to more than 5.3 eV, as hole injection into the blue emitter material at a work function of -5 to -5.1 eV is made
25 extremely difficult, which is considered to be a cause of the instability, and
2. Replacing PSSH with other doping agents, as it is assumed that its sulphonic acid groups lead to the emitter
30 material being damaged during operation.

Both approaches have resulted in certain advances which, however, are still far from adequate.

Therefore there is still a great need for a composition which allows for the manufacture of electronic devices with improved properties and in particular organic light-emitting diodes, wherein the composition provides for a high stability of the
5 RGB emitters including, in particular, blue.

This object is surprisingly achieved by the composition according to any one of claims 1 to 10 or 16.

10 The composition according to the invention is characterized in that it comprises at least one intrinsically conductive polymer and indium.

Surprisingly, in particular organic light-emitting diodes,
15 OLEDs and PLEDs which exhibit high stability and luminous efficacy can be prepared using such a composition.

Intrinsically conductive polymers or conductive polymers are meant to be substances which are built up from low molecular
20 weight compounds (monomers), are at least oligomeric as a result of polymerization, thus contain at least 3 monomer units which are linked by a chemical bond, have a conjugated π -electron system in the neutral (non-conductive) state and can be converted by oxidation, reduction or protonation (which is often
25 referred to as "doping") to an ionic form which is conductive. The conductivity is at least 10^{-7} S/cm and is usually below 10^5 S/cm.

In the case of doping by oxidation there are used as doping
30 agent e.g. iodine, peroxides, Lewis and proton acids or in the case of doping by reduction e.g. sodium, potassium, calcium.

Conductive polymers can vary remarkably in chemical composition. For example, acetylene, benzene, naphthalene, pyrrole, aniline, thiophene, phenylene sulphide, peri-naphthalene and others, as well as their derivatives such as sulpho-aniline, ethylenedioxythiophene, thieno-thiophene and others, as well as their alkyl or alkoxy derivatives or derivatives with other side-groups, such as sulphonate, phenyl and other side-groups, have proved successful monomers. Combinations of the above-mentioned monomers can also be used as monomer. Thus, for example, aniline and phenylene sulphide are coupled and these A-B dimers are then used as monomers. Depending on the objective, e.g. pyrrole, thiophene or alkylthiophenes, ethylenedioxythiophene, thieno-thiophene, aniline, phenylene sulphide and others can be joined together to form A-B structures and these can then be reacted to form oligomers or polymers.

Most conductive polymers display a greater or lesser increase in conductivity with increasing temperature, which identifies them to be non-metallic conductors. Other conductive polymers display, at least in a temperature range close to room temperature, a metallic behaviour inasmuch as conductivity falls as temperature rises. A further method of recognizing metallic behaviour is the plotting of the so-called "reduced activation energy" of conductivity against temperature at low temperatures (down to nearly 0 K). Conductors with a metallic contribution to conductivity display a positive slope of the curve at low temperature. Such substances are referred to as "organic metals".

Preferred intrinsically conductive polymers are those mentioned above. In particular there may be mentioned as examples: polyaniline (PAni), polythiophene (PTh), poly(3,4-ethylenedioxythiophenes) (PEDT), polydiacetylene, 5 polyacetylene (PAC), polypyrrole (PPy), polyisothianaphthene (PITN), polyheteroarylene vinylene (PArV), wherein the heteroarylene group can be e.g. thiophene, furan or pyrrole, poly-p-phenylene (PpP), polyphenylene sulphide (PPS), polyperinaphthalene (PPN), polyphthalocyanine (PPc) and others, 10 as well as their derivatives (which are formed e.g. from monomers substituted with side chains or groups), copolymers thereof and physical mixtures thereof. Particularly preferred are polyaniline (PAni), polythiophene (PTh), polypyrrole (PPy), poly(3,4-ethylenedioxythiophenes) (PEDT), polythienothiophene 15 (PTT) and their derivatives and mixtures thereof.

A good overview of already synthesized intrinsically conductive polymers which are suitable according to the invention can be found in Synthetic Metals, numbers 17, 18 20 and 19 (1987) and vols. 84-86 (1997).

Preferably, the composition according to the invention comprises polyaniline, polythiophene, polypyrrole or derivatives of these as intrinsically conductive polymer. 25 Mixtures are likewise possible. Polyaniline, polythiophene or derivatives thereof and in particular polyaniline (PANI), polypyrrole (Ppy), polythienothiophene (PTT) and poly(3,4-ethylenedioxy-2,5-thiophene (PEDOT) are particularly preferred. The latter is commercially available under the name 30 Baytron.

A composition is further preferred wherein the intrinsically conductive polymer is present in doped form. Low-molecular

weight and in particular polymer-bonded doping agents are suitable as doping agents. The conductive polymer is preferably doped with polystyrene sulphononic acid (PSSH), polyfluorosulphonic acid co-tetrafluoroethylene (commercially available under the name Nafion), poly(vinyl sulphononic acid) and (poly(2-acrylamido-2-methyl-propane sulphononic acid) (PAMPSA), wherein the first two named are particularly preferred.

10 The indium is present in the composition preferably in elemental form or in ionic form. It may be present in particular as an indium salt, such as indium sulphate. Salts are preferred which form with one of the above-named doping agents for the intrinsically conductive polymer. Salts with
15 the named preferred doping agents and in particular indium polystyrene sulphononic acid (In-PSSH) have proved to be particularly preferred.

The composition is usually present as a solid, in particular
20 as a powder. However, it is preferred that the composition is present as a mixture, in particular as a solution or dispersion. These offer substantial advantages in the application and in particular in use for the manufacture of electronic devices.

25 The compositions according to the invention can contain the intrinsically conductive polymer and indium in the form of a simple mixture. They can, however, also contain these components in the form of a chemical compound of intrinsically
30 conductive polymer and indium.

Depending on in particular the polymer selected, the form of the indium used and the reaction conditions, either a simple mixture or surprisingly a chemical compound of intrinsically
35 conductive polymer with indium is formed. Using known analytic

methods a person skilled in the art can control the conditions and the course of the reaction of the materials used to form the composition according to the invention in a desired manner.

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In particular, cyclovoltammetry has been used as a suitable technique to detect the formation of a chemical compound. It was used to demonstrate the formation of a compound of indium and polyaniline, and this compound forms a preferred
10 embodiment of the invention. A further technique with which proof of the formation of a chemical compound of indium and polyaniline was accomplished is UV/Vis spectroscopy.

It has thus far not been possible to explain the nature of the
15 chemical bond between indium and polymer. However, it could possibly be a complex bond.

The composition according to the invention is preferably prepared by a process wherein intrinsically conductive polymer
20 is contacted with indium in the presence of a dispersant or solvent.

It is preferred to contact the intrinsically conductive polymer, particularly in doped form, with an indium compound,
25 in particular an indium salt, or with elemental indium. It is possible that the polymer is already present in dispersed form.

Usually the process is performed such that, after the
30 synthesis of the conductive polymer, as e.g. disclosed in EP 329 768, has been completed, indium metal or indium salt is added to the synthesis solution. After formation of either the mixture or the chemical compound, a work-up is carried out and the obtained material is typically dispersed.

35

Furthermore, a process is also preferred wherein the preparation of the intrinsically conductive polymer is carried out in the presence of an indium compound, such as an indium salt, or of elemental indium. In this embodiment, indium of
5 the selected form is typically added to the mixture of the educts, the reaction of which then leads to the desired polymer.

Moreover, a process according to the invention is preferred
10 wherein the composition is dispersed. Suitable dispersants are in particular aqueous or organic dispersants.

The process serves preferably for the preparation of compounds of polyaniline and indium, wherein in particular doping agents
15 such as PSSH and/or polyfluorosulphonic acid co-tetrafluoroethylene are additionally present.

In cases in which chemical compounds have been formed and not simply physical mixtures of conductive polymers with indium
20 ions, this could be detected by cyclovoltammetry. Because the normal potential of the conductive polymer, and particularly of the preferred polyaniline, has clearly shifted, the formation of a novel compound can be observed. Furthermore in these cases the shift of an absorption peak was observed in
25 the UV/Vis spectrum.

The composition according to the invention and in particular the chemical compounds of polymer and indium according to the invention surprisingly permit the manufacture of electronic
30 devices with attractive properties.

The invention therefore also relates to an electronic device which comprises the composition according to the invention.

A device is preferred which is a light-emitting diode and in particular an organic light-emitting diode OLED.

5 The device preferably comprises the composition in a layer between the electrodes of the light-emitting diode.

One such layer is in particular the so-called hole-injection layer, which is also called charge-injection or buffer layer. It is usually deposited onto the anode of the diode.

10

Thus a device is further preferred wherein the composition is present in the hole-injection layer and in particular forms said layer.

15 Surprisingly hole-injection layers comprising the composition according to the invention and in particular are formed from it, particularly a chemical compound of conductive polymer and indium, preferably of polyaniline and indium, in conjunction with customary polymers as emitter layer or light-emitting
20 layer, such as Super Yellow, allow for a very high stability of the OLED even in pulsed operation.

Even more surprising is the dramatic increase in stability and luminous efficacy in OLEDs with blue light-emitting polymers.
25 Thus, by means of the composition according to the invention it is possible to prepare OLEDs which have no electron-blocking layer between hole-injection layer and emitter layer.

30 Blue-emitting OLEDs could previously not be operated without such a blocking layer, not even when using PEDOT/PSSH, PAni polyfluorosulphonic acid co-tetrafluoroethylene, PTT/PSSH or PTT-polyfluorosulphonic acid co-tetrafluoroethylene as a hole-injection layer. With all these materials the luminous
35 efficacy decreased already after a short time.

Using the composition according to the invention it has become possible for the first time with a specific blue emitter to operate an OLED without blocking layer but with a life of more
5 than 10 hours. Previously this emitter could not be used practically with OLEDs without a blocking layer. With another emitter the use of the composition according to the invention led, in spite of the absence of a blocking layer, to an increase in life to more than 150 hours. On the other hand a
10 corresponding OLED wherein PEDOT was used as hole-injection layer showed a life of less than 100 hours.

The favourable impact of the composition according to the invention in particular on the stability of OLEDs is also
15 surprising because it has been previously assumed that layers in OLEDs must have absolutely no impurities, in particular metallic. For this reason the dispersions used for the preparation of hole-injection layers have always been purified at great cost. Moreover it is surprising that the composition
20 according to the invention has these properties also when the polymer is doped with aromatic sulphonic acids, although a destabilizing effect is ascribed to these same acids.

However, tests with other (polyaniline) compounds, e.g. with
25 Fe or Cu, led to no improvement in stability, but rather, as in the case of compounds with silver, to a deterioration in the properties of the OLEDs.

The invention thus also relates to a process for the
30 manufacture of electronic devices wherein the composition according to the invention is used.

It also relates to the use of the composition for the manufacture of electronic devices, and in particular a use
35 wherein the composition is used as a layer between the

electrodes of a light-emitting diode and in particular as a hole-injection layer.

The invention is described in further detail below with
5 reference to examples.

Examples

Example 1 - Polyaniline PSSH powder

5 Firstly polyaniline powder was prepared according to the
process described in EP 329 768. PANI/PSSH (ratio of monomer
to sulphonic acid groups 1:1.5) was produced by
introducing 1010 g of a 30% solution of polystyrene sulphonic
10 acid (PSSH) and 89 ml aniline in 4190 g deionized water into a
double-walled reactor and cooling the solution to 1°C by means
of a cryostat and cooling medium. A solution of 280 g ammonium
peroxodisulphate (APS) in 420 ml deionized water was added
dropwise to this solution so slowly that the temperature did
not exceed 5°C. The obtained solid was precipitated with
15 acetone, filtered, washed with acetone and dried.

Example 2 - Polyaniline PSSH indium powder type A

20 In analogous manner to Example 1 73.9 g PSSH, 7.44 ml aniline
and 16.3 g indium(II) sulphate in 48.6 ml deionized water were
introduced and reacted with 24 g APS. This was then worked up
analogously to Example 1.

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Example 3 - Polyaniline PSSH indium powder type B

In analogous manner to Example 1 73.9 g PSSH, 7.44 ml aniline
and 944 mg indium granules in 48.6 ml deionized water were
30 introduced and reacted with 24 g APS. Before further
working-up, non-reacted indium granule remains were separated
off. The remaining solid was washed and dried, and a residue
of 685 mg remained.

Example 4

Polyaniline PSSH indium powder type C

5 In analogous manner to Example 1 73.9 g PSSH, 7.44 ml aniline
in 48.6 ml deionized water were introduced and reacted
with 24 g APS. Once the reaction was complete 985 mg indium
granules were added into the reaction mixture and the mixture
was stirred for 22 hours. Before further working-up
10 non-reacted indium granule remains were separated off. The
remaining solid was washed and dried and a residue of 610 mg
remained.

15 Example 5

Dispersion of a powder in water

Firstly the residual humidity of the powder (according to
20 Examples 1-4) was determined in order to be able to determine
a correct weighed-in quantity. Then 16 g powder (from
Example 1, 2, 3 or 4) was added to 500 ml deionized water and
dispersed in the Ultraturrax at a speed of 10,000 rpm for 1.5
hours.

25 The dispersions obtained were then redispersed with ultrasound
by bombarding the vessel with ultrasound (Sonotrode with 1 kW
output) under cooling with water for 30 min .

30 The dispersions had particle size values of 40-80 nm
(numerical average), measured by means of the
double-measurement laser method.

Finally, the dispersions could, if desired, be purified again
35 by means of ion exchange in the usual manner.

Example 6

5 Preparation of a dispersion with subsequent formation of the
indium composition, type 1

A dispersion with powder from Example 1 was prepared according to Example 5. This dispersion was produced with 30 parts of a 30% aqueous solution of polystyrene sulphonic acid (PSSH)
10 which contained indium sulphate in a weight ratio of 1:1.

Example 7

15 Preparation of a dispersion with subsequent formation of the
indium composition, type 2

A dispersion (120 g) with powder from Example 1 was prepared according to Example 5. 650 mg indium granules were added to
20 this dispersion and the dispersion was stirred for 72 hours. It was then filtered over black-band filters. The indium remaining in the filter was washed with deionized water and dried. 563 mg indium remained. The dispersion thus contained 0.72 mg indium per gram of dispersion.

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Example 8

30 Preparation of a dispersion with subsequent formation of the
indium composition, type 3

A dispersion (100 g) with powder from Example 1 was prepared according to Example 5. 20 g of a 15% perfluorosulphonic acid co-tetrafluoroethylene solution in water (Liquion Solution
35 LQ-1115, 110 EW) was added to this dispersion and the

dispersion was stirred for 20 min. The obtained dispersion was then further processed as in Example 7.

Example 9

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Compositions of polypyrrole with indium

To prepare corresponding compositions according to the invention with polypyrrole, Examples 1-5 and 6-8 were
10 analogously reprocessed, wherein (PPy) was used as intrinsically conductive polypyrrole instead of PANI.

Example 10

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Compositions of PEDOT with indium

To prepare corresponding compositions with PEDOT, work was carried out analogously to Examples 6-8 and PEDOT in the form
20 of the commercial product Baytron P AI 4083 was used instead of PANI as intrinsically conductive polymer.

Claims

1. Composition comprising at least one intrinsically conductive polymer and indium.
2. Composition according to claim 1 comprising polyaniline, polythiophene, polypyrrole or derivatives of these as intrinsically conductive polymer.
3. Composition according to claim 2 comprising poly(3,4-ethylenedioxy-2,5-thiophene), polyaniline or polythienothiophene as intrinsically conductive polymer.
4. Composition according to any one of claims 1 to 3 comprising the intrinsically conductive polymer in doped form.
5. Composition according to claim 4, wherein the intrinsically conductive polymer is doped with polystyrene sulphonic acid or polyfluorosulphonic acid co-tetrafluoroethylene.
6. Composition according to any one of claims 1 to 5 comprising indium in elemental form or in ion form.
7. Composition according to claim 6 comprising indium as an indium salt, in particular indium polystyrene sulphonic acid or indium sulphate.
8. Composition according to any one of claims 1 to 7, which is present as a mixture, particularly as a solution or dispersion.

9. Composition according to one of claims 1 to 8, which is a chemical compound of intrinsically conductive polymer and indium.
10. Composition according to claim 9, which is a chemical compound of polyaniline and indium.
11. Process for the preparation of the composition according to any one of claims 1 to 10, wherein intrinsically conductive polymer is contacted with indium in the presence of a dispersant or solvent.
12. Process according to claim 11, wherein intrinsically conductive polymer, particularly in doped form, is contacted with an indium salt.
13. Process according to claim 11, wherein intrinsically conductive polymer, particularly in doped form, is contacted with elemental indium.
14. Process according to claim 11, wherein the intrinsically conductive polymer is prepared in the presence of an indium compound or of elemental indium.
15. Process according to any one of claims 10 to 14, wherein the composition is dispersed.
16. Composition which is obtainable by a process according to any one of claims 11 to 15.
17. Electronic device comprising the composition according to any one of claims 1 to 10 or 16.
18. Device according to claim 17, which is a light-emitting diode.

19. Device according to claim 18, wherein the composition is present in a layer between the electrodes of the light-emitting diode.
20. Device according to claim 19, wherein the composition is present in the hole-injection layer and in particular forms said layer.
21. Process for the manufacture of electronic devices, wherein a composition according to any one of claims 1 to 10 or 16 is used.
22. Use of the composition according to any one of claims 1 to 10 or 16 for the manufacture of electronic devices.
23. Use according to claim 22, wherein the composition is used as a layer between the electrodes of a light-emitting diode and in particular as a hole-injection layer.