

Description

Title of Invention: Method Of Forming A Polythiophene:Polysulfonate Complex

Technical Field

The present invention generally relates to a method of forming a polythiophene:polysulfonate complex. The present invention also relates to a method of forming a film, and the polythiophene:polysulfonate complex and the film made according to the methods as defined herein.

Background Art

Conductive and semi-conductive polymers are rapidly gaining economic significance and attraction in new applications since these polymers have numerous advantages over metals. These layers of conductive polymers have various industrial applications due to their potentially useful properties, including processibility, mechanical flexibility, ionic-electronic transduction, weight and biofunctionality. Examples of known π -conjugated polymers are polythiophenes, polypyrroles, polyanilines and polyacetylenes. These conductive polymers are prepared by chemical or electrochemical oxidative processes from precursors for the preparation of conductive polymers, for example, optionally substituted thiophenes, pyrroles and anilines and their particular derivatives which may be oligomeric. In this regard, chemically oxidative polymerization is prevalent as it can be achieved in a simple fashion in a liquid medium or on various substrates.

Indium tin oxide (ITO) is a commonly used transparent electrode material due to its excellent optoelectronic properties such as high transparency and high conductivity. However, the high vacuum and high temperature requirements for the fabrication of ITO and its mechanical brittleness render it not an ideal transparent electrode choice for flexible polymer solar cells (PSCs). Thus, some promising ITO alternatives including conducting polymers and graphenes have been examined as transparent electrodes for flexible polymer solar cells.

Polyaniline (nanofibers) and poly(p-phenylene vinylene) (PPV) are some examples of commonly used conductive polymers that are commercially available. The popularity is due to their several advantageous properties that include simple acid/base doping/dedoping chemistry, environmental stability, good optoelectronic properties, good stability in its p-doped form, good conductivity and/or good film-forming properties. In this regard, these polymers are being targeted for use as electronic components in applications such as actuators, memory devices, light-emitting diodes (LED) or organic LED, photovoltaic devices, organic microelectronics, nonlinear optic devices, batteries, bio- and chemical-sensors, and organic solar cells. However, some of these conductive polymers are difficult to store and transport due to its instability at room temperature, thus it can be expensive when using these polymers.

The synthesis for these types of polymers can vary from one to another. In this case, it can be a facile synthesis to a lengthy and tedious synthesis, leading to demand that a more efficient and facile synthesis be developed. In addition, fabrication techniques of different polymers are different from one another as well. In this regard, there is a demand for facile formation of alternative conducting polymer material that has a lower cost for storage and transportation of the polymer material. Further to that, there is also a demand to develop a more convenient method for the dispersion of the conducting polymer material and fabrication techniques of the same material onto substrate surfaces.

Accordingly, there is a need for such an alternative conducting polymer material that ameliorates one or more disadvantages mentioned above. There is a need to provide a method of forming such conductive polymer material that ameliorates one or more disadvantages mentioned above.

Summary of Invention

According to a first aspect, there is provided a method of forming a polythiophene:polysulfonate complex comprising the step of reacting a solution mixture of a thiophene and a polysulfonate salt in the presence of a catalyst and an oxidant under conditions to form the polythiophene:polysulfonate complex.

Advantageously, the above method may result in the production of solid polythiophene:polysulfonate complex that can be easily separated from the reaction mixture through standard purification methods such as filtering or centrifuging.

According to a second aspect, there is provided a method of forming a film of a polythiophene:polysulfonate complex on a substrate surface comprising the steps of (a) coating the substrate surface with a dispersion of the polythiophene:polysulfonate complex; and (b) drying the coated polythiophene:polysulfonate complex to form the film.

Advantageously, the polythiophene:polysulfonate complex film may be conductive across a wide range from 10^{-3} to 400 S/cm.

According to a third aspect, there is provided a polythiophene:polysulfonate complex made according to a method as defined herein.

According to a fourth aspect, there is provided a film of a polythiophene:polysulfonate complex made according to a method as defined herein.

Definitions

The following words and terms used herein shall have the meaning indicated:

The term “conductive polymer or semi-conductive polymer” is to be interpreted broadly to include a network of organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semi-conductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, i.e., they are not thermoformable but like insulating polymers, they are organic materials. They can offer high electrical conductivity and optical properties but do not show similar mechanical properties to other commercially available polymers. The

electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

The term "alkyl" as used herein includes straight chain or branched chain saturated aliphatic groups having from 1 to 6 carbon atoms, eg, 1, 2, 3, 4, 5, or 6 carbon atoms. For example, the term alkyl includes, but is not limited to, methyl, ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl and the like.

The term "alkenyl group" as used herein includes straight or branched chain unsaturated aliphatic hydrocarbon groups having from 2 to 6 carbon atoms, eg, 2, 3, 4, 5, or 6 carbon atoms and having at least one double bond, of either *E*, *Z*, *cis* or *trans* stereochemistry where applicable, anywhere in the alkyl chain. Examples of alkenyl groups include but are not limited to ethenyl, vinyl, allyl, 1-methylvinyl, 1-propenyl, 2-propenyl, 2-methyl-1-propenyl, 2-methyl-1-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1,3-butadienyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1,3-pentadienyl, 2,4-pentadienyl, 1,4-pentadienyl, 3-methyl-2-butenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 1,3-hexadienyl, 1,4-hexadienyl, 2-methylpentenyl and the like.

The term "cycloalkyl" as used herein includes cyclic saturated aliphatic groups and refers to saturated, monocyclic, bicyclic, polycyclic or fused polycyclic hydrocarbon radicals having from 3 to 6 carbon atoms, eg, 3, 4, 5, or 6 carbon atoms. Examples of cycloalkyl groups include but are not limited to cyclopropyl, 2-methylcyclopropyl, cyclobutyl, cyclopentyl, 2-methylcyclopentyl, 3-methylcyclopentyl, cyclohexyl, and the like.

The term "aryl" as used herein includes single, polynuclear, conjugated and fused residues of aromatic hydrocarbons having from 6 to 10 carbon atoms. Examples of such groups include phenyl, biphenyl, naphthyl, phenanthrenyl, and the like.

The term "optionally substituted" as used herein means the group to which this term refers may be unsubstituted, or may be substituted with one or more groups independently selected from alkyl, alkenyl, cycloalkyl, or hydroxyl.

The term "sheet resistance" as used herein refers to the measure of resistance of thin films that are nominally uniform in thickness. It is commonly used to characterize materials made by semiconductor doping, metal deposition, resistive paste printing, and glass coating. The utility of sheet resistance as opposed to resistance or resistivity is that it is directly measured using a four-terminal sensing measurement (also known as a four-point probe measurement) or indirectly by using a non-contact eddy current based testing device. Sheet resistance is invariable under scaling of the film contact and therefore can be used to compare the electrical properties of devices that are significantly different in size.

The term "contact angle" as used herein refers to an angle that a liquid creates with a solid surface or capillary walls of a porous material when both materials come in contact together. This angle is determined by both properties of the solid and the liquid, and the interaction and repulsion forces between liquid and solid and by the three phase interface properties (gas, liquid and solid). Those interactions are described by cohesion and adhesion forces which are intermolecular forces. The balance between the cohesive forces of similar molecules such as between the liquid molecules (i.e. hydrogen bonds and Van

der Waals forces) and the adhesive forces between dissimilar molecules such as between the liquid and solid molecules (i.e. mechanical and electrostatic forces) will determine the contact angle created in the solid and liquid interface.

The terms “open circuit voltage (V_{oc})” as used herein refers to the open circuit voltage of the solar cell, which is the maximum voltage that the solar cell will supply; that is the voltage without any load applied.

The terms “short circuit current (I_{sc} or J_{sc})” as used herein refers to the short circuit current of a solar cell, which is the maximum current of the solar under conditions of a zero resistance load; a free flow or zero volt potential drop across the cell.

The terms “fill factor (FF)” as used herein can be calculated based on the formula $FF = I_{Pmax} V_{Pmax} / I_{sc} V_{oc}$, where the numerator ($I_{Pmax} V_{Pmax}$) refers to the maximum power, I_{sc} refers to short circuit current and V_{oc} refers to open circuit voltage.

The terms “power conversion efficiency (PCE)” as used herein refers to the general efficiency of the solar cell; that is the ratio of generated electricity to incoming light energy. The formula for the PCE is $PCE = I_{sc} V_{oc} FF / P_{light}$.

The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

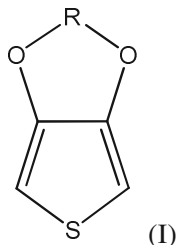
Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Optional Embodiments

Exemplary, non-limiting embodiments of a method of forming a polythiophene:polysulfonate complex will now be disclosed. The method comprises the step of reacting a solution mixture of a thiophene and a polysulfonate salt in the presence of a catalyst and an oxidant under conditions to form the polythiophene:polysulfonate complex.

The method may comprise the step of providing the thiophene as one having the following general formula (I)

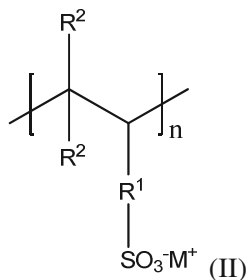


wherein

R is a C₁₋₆-alkylene radical optionally substituted with one or more of C₁₋₆-alkyl, C₂₋₆-alkenyl, C₃₋₆-cycloalkyl or hydroxyl.

Hence, R may be methylene, ethylene, n-propylene, n-butylene, n-pentylene or n-hexylene. The thiophene may be 3,4-ethylenedioxythiophene.

The method may comprise the step of providing the polysulfonate salt as one having the following general formula (II)



wherein

R¹ is selected from the group consisting of a bond, C₁₋₆-alkyl, C₂₋₆-alkenyl, C₃₋₆-cycloalkyl and aryl, wherein said C₁₋₆-alkyl, C₂₋₆-alkenyl, C₃₋₆-cycloalkyl or aryl is optionally substituted with one or more of C₁₋₆-alkyl, C₂₋₆-alkenyl, C₃₋₆-cycloalkyl, or hydroxyl;

R² is independently selected from the group consisting of C₁₋₆-alkyl, C₂₋₆-alkenyl, C₃₋₆-cycloalkyl and hydroxyl;

M⁺ is a cation selected from an alkali metal cation or an ammonium ion (or NH₄⁺); and

n is in the range of 2 to 600.

Where R^1 or R^2 is C_{1-6} -alkyl, the C_{1-6} -alkyl may be selected from methyl, ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, etc. The same applies when C_{1-6} -alkyl is used as a substituent.

Where R^1 or R^2 is C_{2-6} -alkenyl, the C_{2-6} -alkenyl may be selected from ethenyl, vinyl, allyl, 1-methylvinyl, 1-propenyl, 2-propenyl, 2-methyl-1-propenyl, 2-methyl-1-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1,3-butadienyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1,3-pentadienyl, 2,4-pentadienyl, 1,4-pentadienyl, 3-methyl-2-butenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 1,3-hexadienyl, 1,4-hexadienyl, 2-methylpentenyl, etc. The same applies when C_{2-6} -alkenyl is used as a substituent.

Where R^1 or R^2 is C_{3-6} -cycloalkyl, the C_{3-6} -cycloalkyl may be selected from cyclopropyl, 2-methylcyclopropyl, cyclobutyl, cyclopentyl, 2-methylcyclopentyl, 3-methylcyclopentyl, cyclohexyl, etc. The same applies when C_{3-6} -cycloalkyl is used as a substituent.

Where R^1 is aryl, the aryl may be phenyl, biphenyl, naphthyl, phenanthrenyl, etc.

With regard to M^+ , the alkali metal cation may be Li^+ , Na^+ , K^+ , Rb^+ , or Cs^+ .

The polysulfonate salt may be poly(sodium-4-styrenesulfonate), poly(lithium-4-styrenesulfonate), poly(potassium-4-styrenesulfonate), [poly(styrenesulfonate), ammonium salt], etc.

The molecular weight of the polysulfonate salt may be in the range of about 200 to about 1,000,000, about 200 to about 1,000, about 1,000 to about 10,000, about 10,000 to about 100,000, about 100,000 to about 200,000, about 100,000 to about 300,000, about 100,000 to about 400,000, about 100,000 to about 500,000, about 100,000 to about 600,000, about 100,000 to about 700,000, about 100,000 to about 800,000, about 100,000 to about 900,000, 100,000 to about 1,000,000, about 200,000 to about 1,000,000, about 300,000 to about 1,000,000 about 400,000 to about 1,000,000, 500,000 to about 1,000,000, 600,000 to about 1,000,000, 700,000 to about 1,000,000, 800,000 to about 1,000,000 or 900,000 to about 1,000,000 g/mol.

The method may comprise the step of selecting the thiophene and the polysulfonate salt at a molar ratio of 1:0.5 to 1:50, 1:0.5 to 1:1, 1:1 to 1:5, 1:1 to 1:10, 1:1 to 1:20, 1:1 to 1:30, 1:1 to 1:40 or 1:1 to 1:50.

The method may comprise the step of selecting the catalyst as a transition metal salt. The transition metal of the transition metal salt may be a transition metal ion such as an ion of iron, cobalt, nickel, vanadium or zirconium. The transition metal ion may be Fe^{2+} , Fe^{3+} , Co^{2+} , Co^{3+} , Ni^+ , Ni^{2+} , Ni^{3+} , V^{2+} , V^{3+} , V^{4+} , V^{5+} or Zr^{4+} . The anion of the transition metal salt may then be, where appropriate, a halide (chloride, bromide or iodide), a sulphate or phosphate. The catalyst may be added at a concentration of less than 10 mol%, less than 8 mol%, less than 5 mol%, less than 3 mol% or less than 1 mol%.

The method may comprise the step of selecting the oxidant as an ammonium salt. The ammonium salt may be ammonium persulfate. The oxidant may be added at an equivalence

in the range of about 1 to about 10, about 1 to about 7, about 1 to about 5, about 1 to about 3, about 7 to about 10, about 5 to about 10 or about 3 to about 10.

The reacting step of the method may be undertaken in an inert atmosphere. The inert atmosphere may be nitrogen, helium, or argon atmosphere.

The reacting step of the method may be undertaken at a temperature in the range of about 20 °C to about 30 °C, about 20 °C to about 22 °C, about 20 °C to about 24 °C, about 20 °C to about 26 °C, about 20 °C to about 28 °C, about 22 °C to about 30 °C, about 24 °C to about 30 °C, about 26 °C to about 30 °C, or about 28 °C to about 30 °C.

The solution mixture of the thiophene and the polysulfonate salt together with the catalyst and oxidant may be termed as a reaction mixture. The reaction mixture may be stirred for a period of time and at a certain temperature. The reaction mixture may be stirred for a period of time from about 10 hours to about 30 hours, such as from about 20 hours to about 25 hours, or about 24 hours. The temperature may be the same as that above or may be increased when the catalyst and/or oxidant are added to the solution mixture. The temperature of the reaction mixture may be in the range of about 20 °C to about 30 °C. The reaction mixture may be stirred using a stir bar at a rpm in the range of about 500 to 1000 rpm, about 700 rpm to about 800 rpm or about 750 rpm.

The method may further comprise the step of separating the formed polythiophene:polysulfonate complex from the reaction mixture. The separating step may comprise filtering the reaction mixture or centrifuging the reaction mixture and then removing the supernatant.

The method may further comprise the step of washing the separated polythiophene:polysulfonate complex. The polythiophene:polysulfonate complex that is separated from the reaction mixture may be washed with deionized water.

The steps of separating and washing may be repeated a number of times as desired.

The method may further comprise the step of boiling the formed polythiophene:polysulfonate complex in the reaction mixture. The boiling step may take up to 5 hours, up to 4 hours, up to 3 hours, up to 2 hours or up to 1 hour. The heated polythiophene:polysulfonate complex may cool down and may be separated from the reaction mixture. The solution of the reaction mixture may be removed and the final solution may be removed by rotary evaporation under reduced pressure. The step of boiling the formed polythiophene:polysulfonate complex may help to remove the remaining catalyst, oxidant and other impurities that may be present in the reaction mixture.

Exemplary, non-limiting embodiments of a polythiophene:polysulfonate complex will now be disclosed. The polythiophene:polysulfonate complex is made according to the above method.

In the polythiophene:polysulfonate complex, the polythiophene may be uncharged or may be present as a cation (being balanced by the polysulfonate anion).

The polythiophene:polysulfonate complex may be dried and may be in the form of a solid such as pellets. The particle size of the polythiophene:polysulfonate complex may be in the range of about 0.1 μm to about 20 μm , about 0.1 μm to about 1 μm , about 1 μm to about 5

μm , about 1 μm to about 10 μm , about 1 μm to about 15 μm , about 1 μm to about 20 μm , about 5 μm to about 20 μm , about 10 μm to about 20 μm , about 15 μm to about 20 μm .

The polythiophene:polysulfonate complex may be conductive, having a specific conductivity in the range of about 10^{-3} to about 400 S/cm, about 10^{-2} to about 400 S/cm, about 0.1 to about 400 S/cm, about 1 to about 400 S/cm, about 10 to about 400 S/cm, about 100 to about 400 S/cm, about 200 to about 400 S/cm, about 300 to about 400 S/cm, about 10^{-3} to about 10^{-2} S/cm, about 10^{-3} to about 0.1 S/cm, about 10^{-3} to about 1 S/cm, about 10^{-3} to about 10 S/cm, about 10^{-3} to about 100 S/cm, about 10^{-3} to about 200 S/cm, or about 10^{-3} to about 300 S/cm.

Exemplary, non-limiting embodiments of a method of forming a film of a polythiophene:polysulfonate complex on a substrate surface will now be disclosed. The method comprises the steps of (a) coating the substrate surface with a dispersion of the polythiophene:polysulfonate complex; and (b) drying the coated polythiophene:polysulfonate complex to form the film.

The dispersion of the polythiophene:polysulfonate complex may be obtained by adding the polythiophene:polysulfonate complex formed from the method as mentioned above into a suitable medium, such as water. The dispersion may be stirred for a period of time to ensure that the dispersion is evenly mixed before the coating step (a).

The coating step (a) may be undertaken by spin coating, spraying or dip coating. Where spin coating is used, the dispersion may be spun coated onto the substrate surface at a rpm in the range of about 2000 rpm to about 4000 rpm (or about 3000 rpm) for a period of time as long as desired.

The drying step (b) may be undertaken by subjecting the coated polythiophene:polysulfonate complex on the substrate surface to heating. The coated substrate may be placed on hot plate and subject to ambient air. The temperature used during heating may be in the range of about 60 °C to about 180 °C, about 60 °C to about 80 °C, about 60 °C to about 100 °C, about 60 °C to about 120 °C, about 60 °C to about 140 °C, about 60 °C to about 160 °C, about 80 °C to about 180 °C, about 100 °C to about 180 °C, about 120 °C to about 180 °C, about 140 °C to about 180 °C, about 160 °C to about 180 °C. The drying step may be undertaken for a few minutes to about 30 minutes, depending on the heating temperature used. The drying step may result or aid in the annealing of the film to the substrate surface.

The method may further comprise the step of adding an additive to the dispersion. The additives may introduce a desired property to the film or may enhance the conductivity of the film. The additive may be ethylene glycol, or dimethyl sulfoxide (DMSO). The additive may be added at a concentration in the range of about 1 wt% to about 10 wt%, about 3 wt% to about 10 wt%, about 5 wt% to about 10 wt%, about 1 wt% to about 3 wt%, or about 1 wt% to about 5 wt%. The additive may be added to improve the solubility of polythiophene:polysulfonate complex.

The method may further comprise the step of dropping an alcohol onto the coated polythiophene:polysulfonate complex after the coating step (a) but before the drying step (b). The alcohol may be methanol or $\text{CF}_3\text{SO}_3\text{H}$:methanol, that may be used to improve the morphology and electrical conductivity of the polythiophene:polysulfonate complex film.

The temperature used during the dropping step may be in the range of about 80 °C to about 180 °C, about 80 °C to about 100 °C, about 80 °C to about 120 °C, about 80 °C to about 140 °C, about 80 °C to about 160 °C, about 100 °C to about 180 °C about 120 °C to about 180 °C, about 140 °C to about 180 °C or about 160 °C to about 180 °C.

The method may further comprise repeating steps (a) and (b) optionally with the step of adding the additive and/or dropping the alcohol to form a multi-layer film on the substrate surface. Hence, the drying step may aid in the annealing of a newly coated film to the layers that are already present on the substrate.

The substrate used is not particularly limited and an exemplary substrate may be glass, polycarbonate, polyethylene terephthalate, polyethylene naphthalate or polydimethylsiloxane.

Exemplary, non-limiting embodiments of a film of a polythiophene:polysulfonate complex will now be disclosed. The film of the polythiophene:polysulfonate complex is made according to the method as mentioned above.

The polythiophene:polysulfonate film may be conductive, having a specific conductivity in the range of about 10^{-3} to about 400 S/cm, about 10^{-2} to about 400 S/cm, about 0.1 to about 400 S/cm, about 1 to about 400 S/cm, about 10 to about 400 S/cm, about 100 to about 400 S/cm, about 200 to about 400 S/cm, about 300 to about 400 S/cm, about 10^{-3} to about 10^{-2} S/cm, about 10^{-3} to about 0.1 S/cm, about 10^{-3} to about 1 S/cm, about 10^{-3} to about 10 S/cm, about 10^{-3} to about 100 S/cm, about 10^{-3} to about 200 S/cm, or about 10^{-3} to about 300 S/cm.

The polythiophene:polysulfonate film may be formed on the substrate surface at a thickness in the range of about 10 nm to about 100 nm, about 20 nm to about 100 nm, about 30 nm to about 100 nm, about 40 nm to about 100 nm, about 50 nm to about 100 nm, about 60 nm to about 100 nm, about 70 nm to about 100 nm, about 80 nm to about 100 nm, about 90 nm to about 100 nm, about 10 nm to about 90 nm, about 10 nm to about 80 nm, about 10 nm to about 70 nm, about 10 nm to about 60 nm, about 10 nm to about 50 nm about 10 nm to about 40 nm, about 10 nm to about 30 nm, about 10 nm to about 20 nm.

The polythiophene:polysulfonate film may have a transmittance of at least about 75% such that at least 75% of visible light can pass through the film to the substrate below. The transmittance can be at least 80%, at least 85%, at least 90%, or at least 95%.

The polythiophene:polysulfonate film may contain one or more additives that may be added in the method discussed above. Where the polythiophene:polysulfonate film contains additive(s), the resultant film may have an increased hydrophilicity as compared to the same film but without any additive(s). Hence, the contact angle of a water droplet placed on the film (containing additive(s)) may be lesser than 70°, lesser than 60°, lesser than 50°, or lesser than 40°.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1 shows the power conversion efficiency (PCE %) of the commercial product 4083 (Clevios 4083) and the two samples LJ-43 and LJ-31.

Fig. 2 shows photographic images of four samples A–D on polycarbonate (PC) substrate.

Examples

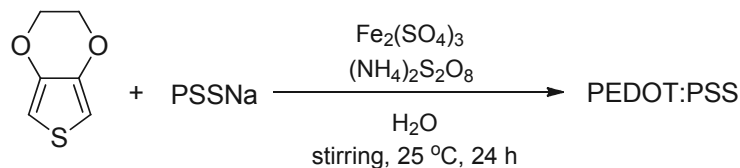
Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Synthetic Details of poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid And Characterization

All chemicals and solvents were purchased from Sigma-Aldrich Corp. (St. Louis, Missouri of the United States of America) and used directly without purification.

Example 1 - Synthesis of poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT:PSS)

Scheme 1 below was used to form the polythiophene:polysulfonate complex from a solution mixture of thiophene and polysulfonate salt in which the thiophene is 3,4-ethylenedioxythiophene (EDOT) and the polysulfonate salt is poly(sodium-4-styrenesulfonate) (PSSNa). The catalyst shown in Scheme 1 below is iron (III) sulfate hydrate while the oxidant used is ammonium persulfate.



Scheme 1

Table 1 thus shows the molecular weights and the amounts of the reactants, catalyst and oxidant used. As shown in Table 1 below, the molar ratio of EDOT:PSSNa used was 1:3

Table 1: Calculation for Sample LJ-31.

	eq.	M.W.	mmol	mass/g
EDOT	1	142.01	5	0.710
PSSNa ⁽¹⁾	3	206.19	15	3.093
Fe ₂ (SO ₄) ₃	0.005	399.88	0.025	0.010
(NH ₄) ₂ S ₂ O ₈	1.3	228.18	6	1.369
H ₂ O				50

⁽¹⁾ Calculation of PSSNa is based on repeating unit.

PSSNa (3.09 g, 15 mmol) was dissolved in water (50 mL) and stirred for 15 minutes, and EDOT (0.71 g, 5 mmol) was added into the PSSNa solution while stirring. The mixture was

then stirred vigorously for 30 minutes at 25 °C under nitrogen. Iron(III) sulfate hydrate (0.010 g, 0.025 mmol) and ammonium persulfate (1.37 g, 6 mmol) were added and the mixture was again stirred using a stir bar at 750 rpm for 24 hours at 25 °C. The mixture was transferred to a centrifuge tube with the aid of 20 mL of water and spun at 4500 rpm for 30 minutes, and the supernatant was decanted. Water (40 mL) was added to the mixture, followed by centrifugation (4500 rpm/30minutes) and decantation. This process was repeated four times. Then 150 mL of water was added and the mixture was placed in an ultrasound bath for 60 minutes, followed by centrifugation and decantation. Finally, another 150 mL of water was added and the mixture was boiled for 2 hours, cooled and then centrifuged again. The supernatant was then drawn off and the final water was removed by rotary evaporation under reduced pressure to obtain the final product PEDOT:PSS.

Further to the above synthesis, several samples were also prepared by modifying the equivalence and molecular weights of reactant PSSNa while maintaining the concentrations of other reagents. Sample LJ-43 was prepared with 1.5 equivalence of PSSNa that has a molecular weight of approximately 70,000. Samples LJ-47 and 48 were prepared with 1.8 equivalence of PSSNa but with different molecular weights and they are approximately 500,000 and 300,000 respectively. Sample LJ-49 was prepared with 2.5 equivalence of PSSNa that has a molecular weight of approximately 300,000. Sample LJ-50 was prepared with 2 equivalence of PSSNa that has a molecular weight of approximately 1,000,000.

Table 2: Calculation for Samples LJ-43, 47, 48, 49 and 50.

Sample ^a	EDOT		PSSNa			(NH ₄) ₂ S ₂ O ₈		H ₂ O
	equiv.	mass (g)/ mmol	MW	equiv.	mass (g)/ mmol	equiv.	mass (g)/ mmol	mL
LJ-43	1.0	0.995/ 7	70,000	1.8	2.165/ 10.5	1.3	2.076/ 9.1	80
LJ-47	1.0	0.4976/ 3.5	500,000	1.8	1.299/ 6.3	1.3	1.027/ 4.5	80
LJ-48	1.0	0.4976/ 3.5	300,000	1.8	1.299/ 6.3	1.3	1.027/ 4.5	80
LJ-49	1.0	0.4976/ 3.5	300,000	2.5	1.804/ 8.75	1.3	1.027/ 4.5	80
LJ-50	1.0	0.995/ 7	1,000,000	2.0	2.886/ 14	1.3	2.076/ 9.1	150

^(a) 1 mg of Fe₂(SO₄)₃ was added to all the samples.

Example 2 – Fabrication process of poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT:PSS) film

PEDOT:PSS Solution Formation and Film Fabrication:

The PEDOT:PSS complex as produced from Example 1 above was suspended in water and stirred overnight. The dispersion of the PEDOT:PSS complex was ultra-sonicated (5W, 2 to 5 minutes) and filtered through a syringe filter (0.45 µm pore size) to remove any large particles. Where noted, 1-2% by weight PSS was added to the PEDOT:PSS solution. The solution was placed on a shaker for at least one hour to ensure good mixing before coating onto a substrate via spin-coating. The solutions were spun coated onto clean substrates (glass or PDMS) at 3000 rpm for 60 seconds. The coated substrates were then subjected to a drying step by placing on a

hot plate in ambient air for 5 minutes at 120 °C to dry. The process was repeated after the films were dried to obtain multi-layer films.

Where desired, an alcohol such as methanol or $\text{CF}_3\text{SO}_3\text{H}$: methanol may be dropped onto the coated complex, whether on the first layer or subsequent layer. This dropping of the alcohol is thus hereafter referred as the 'drop' method. Here, 120 mL of methanol or $\text{CF}_3\text{SO}_3\text{H}$: methanol (1:10) was dropped on the film at 120 °C before drying (or annealing); and the annealing process was continued for 15 minutes. Thicker PEDOT:PSS films were prepared by multiple spin coating and annealing processes. Finally, the film treatments were conducted after each layer is completed. In order to achieve multi-layers film, the annealing process was carried out for 5 minutes after each layer is completed.

The substrate with the formed film(s) was then subjected to characterization tests such as sheet resistance measurement and UV/Vis measurement.

The sheet resistance measurements of PEDOT:PSS thin films were performed with a Loresta EP sheet resistance meter NSX-2100V with a four probe setup. UV/Vis measurements were performed with a Shimadzu UV-3600 apparatus with an integrating sphere setup (300 to 800 nm).

Table 3 shows the various samples with their respective spin rates, the % transparency and the sheet resistance derived from the various different methods – spin coating, drop method using methanol and drop method in acid using $\text{CF}_3\text{SO}_3\text{H}$:methanol.

Table 3: Results of various films

Sample	Spin rate	Tran (%)	Sheet R (Ω/sq)	Sheet R (Ω/sq) Drop Meth	Sheet R (Ω/sq) Dip in Acid M
31 (3, 7.06%) 2% PSS 1L	3000 rpm	88	1.8M	700	450
43 (1.8)	3000 rpm		1.6M	2.3k	1.5k
47-1 (1.8, 2%) 0.5MMw 1%pss 2L	3000 rpm		1.3M	19k	8k
48-1 (1.8, 2%) 0.3MMw 2L	3000 rpm		0.7M	13k	6.3k
48-1 (1.8, 2%) 1PSS 4L US	3000 rpm		over	5.5k	3.4-3.5k
49 1%pss 3L	3000 rpm		over	11k	8k
50 1%pss 1L	3000 rpm		over	8k	5.1k
50 1%pss 2L	3000 rpm		over	5k	4k
50 1L	3000 rpm		5M	6.5k	5k

All samples were spun coated on glass substrates at a spin rate of 3000 rpm. Sample LJ-31 is 88% transparent with glass and had a 450 Ω/sq sheet resistance whereas Samples LJ-47-

1, LJ-48-1(2L), LJ-48-1(4L), LJ-49, LJ-50(1%PSS-1L), LJ-50(1%PSS-2L) and LJ-50(1L) were in the range of 3400 to 8000 Ω/sq .

Example 3 – Application process of poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT:PSS) films

Three types of PEDOT:PSS films were used as hole transport layers (HTL) in an organic photodetector (OPD). The three samples were analysed (Clevios 4083, LJ-43, LJ-31) and their performances are tabulated in Table 4 below. The three samples were of a thickness of 40 nm and were used in the organic photodetector.

Table 4: Performance of the films in an organic photodetector

PEDOT-PSS	PCE (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)
4083 (commercial)	6.12	0.785	12.31	63.34
LJ-43	6.21	0.797	12.77	61.01
LJ-31	5.91	0.788	12.68	59.12

Based on the above table together with Fig. 1, the commercially available product 4083 had a power conversion efficiency (PCE %) of 6.12 as compared to sample LJ-43 that had an efficiency of 6.21. Further to that, sample LJ-43 had an open-circuit voltage (V_{oc}) of 0.797 that was higher than 0.785 of Sample 4083. Similarly, sample LJ-43 had a current density (J_{sc}) of 12.77, which was higher than 12.31 of Sample 4083. In this regard, sample LJ-43 has an improved performance when used in the organic photodetector than sample 4083. Further to the above results, Table 5 below shows the conductivity of Sample LJ-43 that ranged from 10^{-3} to 400 S/cm and transparent% of 88% when inclusive of substrate and up to 94.5% when the substrate is excluded. The thickness of the PEDOT:PSS film is 40 nm.

Table 5: Parameters of Sample LJ-43

	Conductivity (S/cm)	T% (400-800nm)	
		Include substrate	Exclude substrate
Solid Pedot	10^{-3} -400	88	94.5

Example 4– Effect of Sample LJ-31 and their Contact Angles

Fig. 2 shows photographic images of four different samples A–D on polycarbonate (PC) substrate, wherein Sample A corresponds to Sample LJ-31 as described above.

Table 6 compares between samples A–D and their respective contact angle with the PC film. Sample A (Sample LJ-31) without any additive has the highest contact angle with the PC film as compared to Samples B–D that had 3% of additives B–D respectively. Sample C has the lowest contact angle of 50° with the PC film. In this regard, additive B corresponds to 3% of ethylene glycol, whereas additive C corresponds to 3% of dimethyl sulfoxide and additive D corresponds to 3% of methanol.

Table 6: Samples A–D and their contact angles with PC film

Sample ID	Contact angle with PC film
Sample A (no additive)	78°
Sample B (3% additive B)	56°
Sample C (3% additive C)	50°
Sample D (3% additive D)	65°

Industrial Applicability

The polythiophene:polysulfonate complex may be used as a conductive polymeric thin film and may be used in a variety of applications such as polymer solar cells (PSCs), biosensors, implantable electrodes or an electrode in capacitors, organic microelectronics and as a conducting layer in through-hole plating. It may be used as a transparent, conductive polymer with high ductility in a wide range of applications.

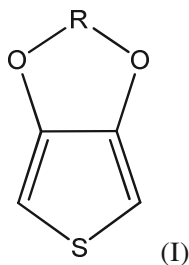
The polythiophene:polysulfonate complex may be used as aqueous solutions or dispersions of PEDOT:PSS polymers that exhibits high electrical conductivity together with low absorption of visible light and high absorption to infrared radiation. Aqueous solutions or dispersions of PEDOT:PSS polymers may be applied to a wide variety of rigid and flexible substrates, e.g. glass and polycarbonate (PC). The thin, extensively-stretched layer of virtually transparent and colorless PEDOT:PSS film may be used as an antistatic agent to prevent electrostatic discharges during production and normal film use. The PEDOT:PSS film may also be applied as antistatic coatings for a wide array of products such as photographic film, thermographic recording materials and photothermographic recording materials, in smart windows, in electrochromic devices, in sensors for organic and bio-organic materials, in field effect transistors, in printing plates, in conductive resin adhesives and in free-standing electrically conductive films.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A method of forming a polythiophene:polysulfonate complex comprising the step of reacting a solution mixture of a thiophene and a polysulfonate salt in the presence of a catalyst and an oxidant under conditions to form said polythiophene:polysulfonate complex.

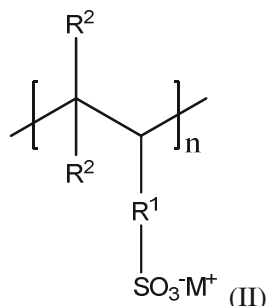
2. The method according to claim 1, comprising the step of providing said thiophene having a general formula (I)



wherein

R is a C₁₋₆-alkylene radical optionally substituted with one or more of C₁₋₆-alkyl, C₂₋₆-alkenyl, C₃₋₆-cycloalkyl or hydroxyl.

3. The method according to claim 1 or 2, comprising the step of providing said polysulfonate salt having a general formula (II)



wherein

R¹ is selected from the group consisting of a bond, C₁₋₆-alkyl, C₂₋₆-alkenyl, C₃₋₆-cycloalkyl and aryl, wherein said C₁₋₆-alkyl, C₂₋₆-alkenyl, C₃₋₆-cycloalkyl or aryl is optionally substituted with one or more of C₁₋₆-alkyl, C₂₋₆-alkenyl, C₃₋₆-cycloalkyl, aryl or hydroxyl;

R² is independently selected from the group consisting of C₁₋₆-alkyl, C₂₋₆-alkenyl, C₃₋₆-cycloalkyl and hydroxyl;

M⁺ is a cation selected from an alkali metal cation or an ammonium ion; and

n is in the range of 2 to 600.

4. The method according to any one of the preceding claims, comprising the step of selecting said thiophene and said polysulfonate salt at a molar ratio of 1:1 to 1:3.

5. The method according to any one of the preceding claims, wherein said catalyst is a transition metal salt.

6. The method according to any one of the preceding claims, wherein said oxidant is an ammonium salt.

7. The method according to any one of the preceding claims, wherein said reacting step is undertaken in an inert atmosphere.

8. The method according to any one of the preceding claims, wherein said reacting step is undertaken in a temperature in the range of 20 °C to 30 °C.

9. The method according to any one of the preceding claims, further comprising the step of separating the formed polythiophene:polysulfonate complex from the reaction.

10. The method according to claim 9, further comprising the step of washing the separated polythiophene:polysulfonate complex.

11. A polythiophene:polysulfonate complex made according to the method of any one of the preceding claims.

12. A method of forming a film of a polythiophene:polysulfonate complex on a substrate surface comprising the steps of:

(a) coating said substrate surface with a dispersion of said polythiophene:polysulfonate complex; and

(b) drying said coated polythiophene:polysulfonate complex to form said film.

13. The method according to claim 12, further comprising the step of adding an additive to said dispersion.

14. The method according to claim 12 or 13, further comprising the step of dropping an alcohol onto said coated polythiophene:polysulfonate complex after said coating step (a) but before said drying step (b).

15. The method according to any one of claims 12 to 14, further comprising repeating the steps as defined in claim 12 optionally with any one of claim 13 or 14 to form a multi-film layer on said substrate surface.

16. A film of a polythiophene:polysulfonate complex made according to the method of any one of claims 12 to 15.