(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
28 January 2010 (28.01.2010)

PCT

(10) **International Publication Number**
WO 2010/011368 A1

(51) **International Patent Classification**: ***H01B 1/12*** (2006.01)

(21) **International Application Number**: PCT/US2009/035079

(22) **International Filing Date**: 25 February 2009 (25.02.2009)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
PCT/US2008/070718 22 July 2008 (22.07.2008) US

(71) **Applicant** *(for all designated States except US)*: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) **Inventors; and**

(75) **Inventors/Applicants** *(for US only)*: **HSU, Che-Hsiung** [US/US]; 4803 Mermaid Boulevard, Wilmington, Delaware 19808 (US). **MENG, Hong** [CN/US]; 104 Shrewsbury Drive, Wilmington, Delaware 19810 (US). **SKULASON, Hjalti** [IS/US]; 546 Blue Blossom Way, Buellton, California 93427 (US). **ZIEBARTH, Jonathan, M.** [US/US]; 2070 East Valley Road, Santa Barbara, California 93108 (US).

(74) **Agent**: **LAMMING, John, H.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

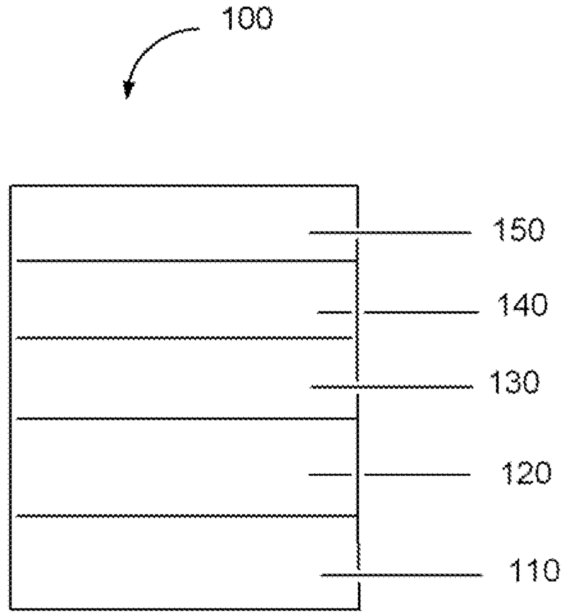
(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, 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, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ,

[Continued on next page]

(54) Title: AQUEOUS DISPERSIONS OF ELECTRICALLY CONDUCTING POLYMERS CONTAINING INORGANIC NANOPARTICLES

FIGURE 1



(57) **Abstract**: The present invention relates to electrically conductive polymer compositions, and their use in electronic devices. The compositions contain an aqueous dispersion of at least one electrically conductive polymer doped with at least one highly-fluorinated acid polymer, and inorganic nanoparticles.

WO 2010/011368 A1

TM), European (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, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

TITLE

AQUEOUS DISPERSIONS OF ELECTRICALLY CONDUCTING POLYMERS CONTAINING INORGANIC NANOPARTICLES

CROSS REFERENCE TO RELATED APPLICATIONS

This is a Continuation-In-Part of Application Serial No. 12/177,359, filed on July 22, 2008, which claims priority to Provisional Application Serial No. 60/952,372, filed on July 27, 2007, both of which are incorporated herein by reference in their entirety.

BACKGROUND INFORMATION

Field of the Disclosure

This disclosure relates in general to electrically conductive polymer compositions containing inorganic nanoparticles, and their use in electronic devices.

Description of the Related Art

Electronic devices define a category of products that include an active layer. Organic electronic devices have at least one organic active layer. Such devices convert electrical energy into radiation such as light emitting diodes, detect signals through electronic processes, convert radiation into electrical energy, such as photovoltaic cells, or include one or more organic semiconductor layers.

Organic light-emitting diodes (OLEDs) are an organic electronic device comprising an organic layer capable of electroluminescence. OLEDs containing conducting polymers can have the following configuration:

anode/buffer layer/EL material/cathode

with additional layers between the electrodes. The anode is typically any material that has the ability to inject holes into the EL material, such as, for example, indium/tin oxide (ITO). The anode is optionally supported on a glass or plastic substrate. EL materials include fluorescent compounds, fluorescent and phosphorescent metal complexes, conjugated polymers, and mixtures thereof. The cathode is typically any material (such as, e.g., Ca or Ba) that has the ability to inject electrons into the EL material. Electrically conducting polymers having low conductivity in the range of 10^{-3} to 10^{-7}S/cm are commonly used as the buffer layer in direct contact with an electrically conductive, inorganic oxide anode such as ITO.

There is a continuing need for improved buffer layer materials.

SUMMARY

There is provided a composition comprising an aqueous dispersion of at least one electrically conductive polymer doped with at least one highly-fluorinated acid polymer, and having inorganic nanoparticles dispersed therein.

In another embodiment, there is provided a film formed from the above composition.

In another embodiment, electronic devices comprising at least one layer comprising the above film are provided.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is illustrated by way of example and not limitation in the accompanying figures.

Figure 1 is a schematic diagram of an organic electronic device.

Skilled artisans will appreciate that objects in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the objects in the figures may be exaggerated relative to other objects to help to improve understanding of embodiments.

DETAILED DESCRIPTION

Many aspects and embodiments are described herein and are merely exemplary and not limiting. After reading this specification, skilled artisans will appreciate that other aspects and embodiments are possible without departing from the scope of the invention.

Other features and benefits of any one or more of the embodiments will be apparent from the following detailed description, and from the claims. The detailed description first addresses Definitions and Clarification of Terms followed by the Electrically Conductive Polymer, the

Highly-fluorinated Acid Polymer, the Inorganic Nanoparticles, Preparation of the Doped Electrically Conductive Polymer Composition, Buffer Layers, Electronic Devices, and finally, Examples.

1. Definitions and Clarification of Terms Used in the Specification and Claims

Before addressing details of embodiments described below, some terms are defined or clarified.

The term "conductor" and its variants are intended to refer to a layer material, member, or structure having an electrical property such that current flows through such layer material, member, or structure without a substantial drop in potential. The term is intended to include semiconductors. In some embodiments, a conductor will form a layer having a conductivity of at least 10^{-7}S/cm.

The term "electrically conductive" as it refers to a material, is intended to mean a material which is inherently or intrinsically capable of electrical conductivity without the addition of carbon black or conductive metal particles.

The term "polymer" is intended to mean a material having at least one repeating monomeric unit. The term includes homopolymers having only one kind, or species, of monomeric unit, and copolymers having two or more different monomeric units, including copolymers formed from monomeric units of different species.

The term "acid polymer" refers to a polymer having acidic groups.

The term "acidic group" refers to a group capable of ionizing to donate a hydrogen ion to a Brønsted base.

The term "highly-fluorinated" refers to a compound in which at least 90% of the available hydrogens bonded to carbon have been replaced by fluorine.

The terms "fully-fluorinated" and "perfluorinated" are used interchangeably and refer to a compound where all of the available hydrogens bonded to carbon have been replaced by fluorine.

The composition may comprise one or more different electrically conductive polymers and one or more different highly-fluorinated acid polymers.

The term "doped" as it refers to an electrically conductive polymer, is intended to mean that the electrically conductive polymer has a polymeric counterion to balance the charge on the conductive polymer.

The term "doped conductive polymer" is intended to mean the conductive polymer and the polymeric counterion that is associated with it.

The term "layer" is used interchangeably with the term "film" and refers to a coating covering a desired area. The term is not limited by size. The area can be as large as an entire device or as small as a specific functional area such as the actual visual display, or as small as a single sub-pixel. Layers and films can be formed by any conventional deposition technique, including vapor deposition, liquid deposition (continuous and discontinuous techniques), and thermal transfer.

The term "nanoparticle" refers to a material having a particle size less than 100 nm. In some embodiments, the particle size is less than 10 nm. In some embodiments, the particle size is less than 5 nm.

The term "aqueous" refers to a liquid that has a significant portion of water, and in one embodiment it is at least about 40% by weight water; in some embodiments, at least about 60% by weight water.

The term "hole transport" when referring to a layer, material, member, or structure, is intended to mean such layer, material, member, or structure facilitates migration of positive charges through the thickness of such layer, material, member, or structure with relative efficiency and small loss of charge.

The term "electron transport" means when referring to a layer, material, member or structure, such a layer, material, member or structure that promotes or facilitates migration of negative charges through such a layer, material, member or structure into another layer, material, member or structure.

The term "organic electronic device" is intended to mean a device including one or more semiconductor layers or materials. Organic electronic devices include, but are not limited to: (1) devices that convert electrical energy into radiation (e.g., a light-emitting diode, light emitting diode display, diode laser, or lighting panel), (2) devices that detect signals through electronic processes (e.g., photodetectors photoconductive cells, photoresistors, photoswitches, phototransistors, phototubes, infrared ("IR") detectors, or biosensors), (3) devices that convert radiation into electrical energy (e.g., a photovoltaic device or solar cell), and (4) devices that include one or more electronic components that include one or more organic semiconductor layers (e.g., a transistor or diode).

As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, use of "a" or "an" are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

Group numbers corresponding to columns within the Periodic Table of the elements use the "New Notation" convention as seen in the *CRC Handbook of Chemistry and Physics*, 81st Edition (2000-2001).

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In the Formulae, the letters Q, R, T, W, X, Y, and Z are used to designate atoms or groups which are defined within. All other letters are used to designate conventional atomic symbols. Group numbers corresponding to columns within the Periodic Table of the elements use the "New Notation" convention as seen in the *CRC Handbook of Chemistry and Physics*, 81st Edition (2000).

To the extent not described herein, many details regarding specific materials, processing acts, and circuits are conventional and may be found in textbooks and other sources within the organic light-emitting diode display, lighting source, photodetector, photovoltaic, and semiconductive member arts.

2. Electrically Conductive Polymers

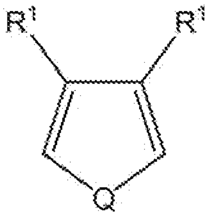
Any electrically conductive polymer can be used in the new composition. In some embodiments, the electrically conductive polymer will form a film which has a conductivity greater than 10^{-7} S/cm.

The conductive polymers suitable for the new composition are made from at least one monomer which, when polymerized alone, forms an electrically conductive homopolymer. Such monomers are referred to herein as "conductive precursor monomers." Monomers which, when polymerized alone form homopolymers which are not electrically conductive, are referred to as "non-conductive precursor monomers." The conductive polymer can be a homopolymer or a copolymer. Conductive copolymers suitable for the new composition can be made from two or more conductive precursor monomers or from a combination of one or more conductive precursor monomers and one or more non-conductive precursor monomers.

In some embodiments, the conductive polymer is made from at least one conductive precursor monomer selected from thiophenes, pyrroles, anilines, and polycyclic aromatics. The term "polycyclic aromatic" refers to compounds having more than one aromatic ring. The rings may be joined by one or more bonds, or they may be fused together. The term "aromatic ring" is intended to include heteroaromatic rings. A "polycyclic heteroaromatic" compound has at least one heteroaromatic ring.

In some embodiments, the conductive polymer is made from at least one precursor monomer selected from thiophenes, selenophenes, tellurophenes, pyrroles, anilines, and polycyclic aromatics. The polymers made from these monomers are referred to herein as polythiophenes, poly(selenophenes), poly(tellurophenes), polypyrroles, polyanilines, and polycyclic aromatic polymers, respectively. The term "polycyclic aromatic" refers to compounds having more than one aromatic ring. The rings may be joined by one or more bonds, or they may be fused together. The term "aromatic ring" is intended to include heteroaromatic rings. A "polycyclic heteroaromatic" compound has at least one heteroaromatic ring. In some embodiments, the polycyclic aromatic polymers are poly(thienothiophenes).

In some embodiments, monomers contemplated for use to form the electrically conductive polymer in the new composition comprise Formula I below:



(I)

wherein:

Q is selected from the group consisting of S, Se, and Te;

R^1 is independently selected so as to be the same or different at each occurrence and is selected from hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkythio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, aryl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, cyano, hydroxyl, epoxy, silane, siloxane, alcohol, benzyl, carboxylate, ether, ether carboxylate, amidosulfonate, ether sulfonate, ester sulfonate, and urethane; or both R^1 groups together may form an alkylene or alkenylene chain completing a 3, 4, 5, 6, or 7-membered aromatic or alicyclic ring, which ring may optionally include one or more divalent nitrogen, selenium, tellurium, sulfur or oxygen atoms.

As used herein, the term "alkyl" refers to a group derived from an aliphatic hydrocarbon and includes linear, branched and cyclic groups which may be unsubstituted or substituted. The term "heteroalkyl" is intended to mean an alkyl group, wherein one or more of the carbon atoms within the alkyl group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like. The term "alkylene" refers to an alkyl group having two points of attachment.

As used herein, the term "alkenyl" refers to a group derived from an aliphatic hydrocarbon having at least one carbon-carbon double bond, and includes linear, branched and cyclic groups which may be unsubstituted or substituted. The term "heteroalkenyl" is intended to mean an alkenyl group, wherein one or more of the carbon atoms within the alkenyl group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like. The term "alkenylene" refers to an alkenyl group having two points of attachment.

As used herein, the following terms for substituent groups refer to the formulae given below:

"alcohol"	$-R^3-OH$
"amido"	$-R^3-C(O)N(R^6)\ R^6$
"amidosulfonate"	$-R^3-C(O)N(R^6)\ R^4-\ SO_3Z$
"benzyl"	$-CH_2-C_6H_5$
"carboxylate"	$-R^3-C(O)O-Z$ or $-R^3-O-C(O)-Z$
"ether"	$-R^3-(O-R^5)_p-O-R^5$
"ether carboxylate"	$-R^3-O-R^4-C(O)O-Z$ or $-R^3-O-R^4-O-C(O)-Z$
"ether sulfonate"	$-R^3-O-R^4-SO_3Z$
"ester sulfonate"	$-R^3-O-C(O)-R^4-SO_3Z$
"sulfonimide"	$-R^3-SO_2-NH-\ SO_2-R^5$
"urethane"	$-R^3-O-C(O)-N(R^6)_2$

where all "R" groups are the same or different at each occurrence and:

R^3 is a single bond or an alkylene group

R^4 is an alkylene group

R^5 is an alkyl group

R^6 is hydrogen or an alkyl group

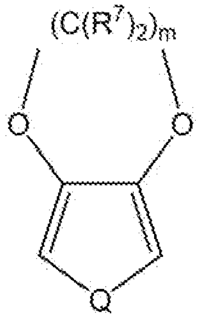
p is 0 or an integer from 1 to 20

Z is H, alkali metal, alkaline earth metal, $N(R^5)_4$ or R^5

Any of the above groups may further be unsubstituted or substituted, and any group may have F substituted for one or more hydrogens, including perfluorinated groups. In some embodiments, the alkyl and alkylene groups have from 1-20 carbon atoms.

In some embodiments, in the monomer, both R^1 together form —W-$(CY^1Y^2)_m$-W- , where m is 2 or 3, W is O, S, Se, PO, NR^6, Y^1 is the same or different at each occurrence and is hydrogen or fluorine, and Y^2 is the same or different at each occurrence and is selected from hydrogen, halogen, alkyl, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, ester sulfonate, and urethane, where the Y groups may be partially or fully fluorinated. In some embodiments, all Y are hydrogen. In some embodiments, the polymer is poly(3,4-ethylenedioxythiophene). In some embodiments, at least one Y group is not hydrogen. In some embodiments, at least one Y group is a substituent having F substituted for at least one hydrogen. In some embodiments, at least one Y group is perfluorinated.

In some embodiments, the monomer has Formula I(a):



(Ia)

wherein:

Q is selected from the group consisting of S, Se, and Te;

R^7 is the same or different at each occurrence and is selected from hydrogen, alkyl, heteroalkyl, alkenyl, heteroalkenyl, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, ester sulfonate, and urethane, with the proviso that at least one R^7 is not hydrogen, and

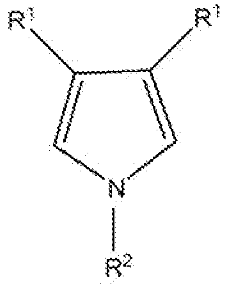
m is 2 or 3.

In some embodiments of Formula I(a), m is two, one R^7 is an alkyl group of more than 5 carbon atoms, and all other R^7 are hydrogen.
In some embodiments of Formula I(a), at least one R^7 group is fluorinated. In some embodiments, at least one R^7 group has at least one fluorine substituent. In some embodiments, the R^7 group is fully fluorinated.

In some embodiments of Formula I(a), the R^7 substituents on the fused alicyclic ring on the monomer offer improved solubility of the monomers in water and facilitate polymerization in the presence of the fluorinated acid polymer.

In some embodiments of Formula I(a), m is 2, one R^7 is sulfonic acid-propylene-ether-methylene and all other R^7 are hydrogen. In some embodiments, m is 2, one R^7 is propyl-ether-ethylene and all other R^7 are hydrogen. In some embodiments, m is 2, one R^7 is methoxy and all other R^7 are hydrogen. In some embodiments, one R^7 is sulfonic acid difluoromethylene ester methylene ($-CH_2-O-C(O)-CF_2-SO_3H$), and all other R^7 are hydrogen.

In some embodiments, pyrrole monomers contemplated for use to form the electrically conductive polymer in the new composition comprise Formula II below.



(II)

where in Formula II:

R^1 is independently selected so as to be the same or different at each occurrence and is selected from hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkythio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, aryl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, cyano, hydroxyl, epoxy, silane, siloxane, alcohol, benzyl, carboxylate, ether, amidosulfonate, ether carboxylate, ether sulfonate, ester sulfonate, and urethane; or both R^1 groups together may form an alkylene or alkenylene chain completing a 3, 4, 5, 6, or 7-membered aromatic or alicyclic ring, which ring may optionally include one or more divalent nitrogen, sulfur, selenium, tellurium, or oxygen atoms; and

R^2 is independently selected so as to be the same or different at each occurrence and is selected from hydrogen, alkyl, alkenyl, aryl, alkanoyl, alkylthioalkyl, alkylaryl, arylalkyl, amino, epoxy, silane, siloxane, alcohol, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, ester sulfonate, and urethane.

In some embodiments, R^1 is the same or different at each occurrence and is independently selected from hydrogen, alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alcohol, benzyl, carboxylate, ether, amidosulfonate, ether carboxylate, ether sulfonate, ester sulfonate, urethane, epoxy, silane, siloxane, and alkyl substituted with one or more of sulfonic acid, carboxylic acid, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, cyano, hydroxyl, epoxy, silane, or siloxane moieties.

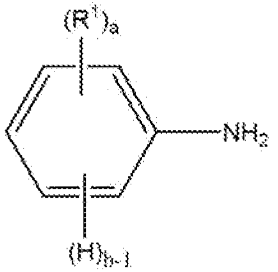
In some embodiments, R^2 is selected from hydrogen, alkyl, and alkyl substituted with one or more of sulfonic acid, carboxylic acid, acrylic acid, phosphoric acid, phosphonic acid, halogen, cyano, hydroxyl, epoxy, silane, or siloxane moieties.

In some embodiments, the pyrrole monomer is unsubstituted and both R^1 and R^2 are hydrogen.

In some embodiments, both R^1 together form a 6- or 7-membered alicyclic ring, which is further substituted with a group selected from alkyl, heteroalkyl, alcohol, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, ester sulfonate, and urethane. These groups can improve the solubility of the monomer and the resulting polymer. In some embodiments, both R^1 together form a 6- or 7-membered alicyclic ring, which is further substituted with an alkyl group. In some embodiments, both R^1 together form a 6- or 7-membered alicyclic ring, which is further substituted with an alkyl group having at least 1 carbon atom.

In some embodiments, both R^1 together form $-O-(CHY)_m-O-$, where m is 2 or 3, and Y is the same or different at each occurrence and is selected from hydrogen, alkyl, alcohol, benzyl, carboxylate, amidosulfonate, ether, ether carboxylate, ether sulfonate, ester sulfonate, and urethane. In some embodiments, at least one Y group is not hydrogen. In some embodiments, at least one Y group is a substituent having F substituted for at least one hydrogen. In some embodiments, at least one Y group is perfluorinated.

In some embodiments, aniline monomers contemplated for use to form the electrically conductive polymer in the new composition comprise Formula III below.



(III)

wherein:

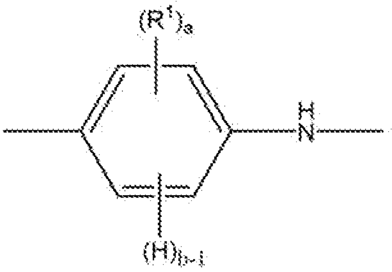
a is 0 or an integer from 1 to 4;

b is an integer from 1 to 5, with the proviso that a + b = 5; and

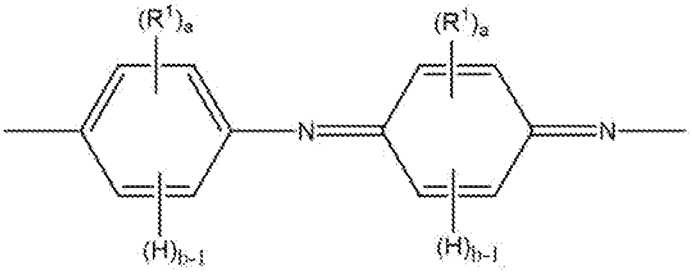
R^1 is independently selected so as to be the same or different at each occurrence and is selected from hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkythio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, aryl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, cyano, hydroxyl, epoxy, silane, siloxane, alcohol, benzyl, carboxylate, ether, ether carboxylate, amidosulfonate, ether sulfonate, ester sulfonate, and urethane; or both R^1 groups together may form an alkylene or alkenylene chain completing a 3, 4, 5, 6, or

7-membered aromatic or alicyclic ring, which ring may optionally include one or more divalent nitrogen, sulfur or oxygen atoms.

When polymerized, the aniline monomeric unit can have Formula IV(a) or Formula IV(b) shown below, or a combination of both formulae.



IV(a)



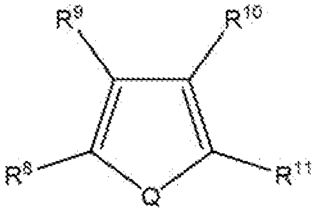
IV(b)

where a, b and R^1 are as defined above.

In some embodiments, the aniline monomer is unsubstituted and a = 0.

In some embodiments, a is not 0 and at least one R^1 is fluorinated. In some embodiments, at least one R^1 is perfluorinated.

In some embodiments, fused polycylic heteroaromatic monomers contemplated for use to form the electrically conductive polymer in the new composition have two or more fused aromatic rings, at least one of which is heteroaromatic. In some embodiments, the fused polycyclic heteroaromatic monomer has Formula V:



(V)

wherein:

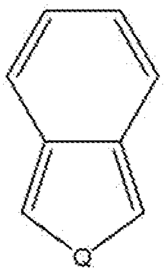
Q is S, Se, Te, or NR^6;

R^6 is hydrogen or alkyl;

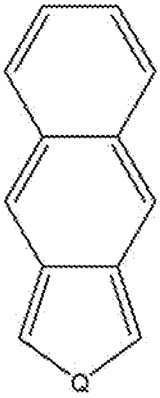
R^8, R^9, R^{10}, and R^{11} are independently selected so as to be the same or different at each occurrence and are selected from hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkythio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, aryl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, nitrile, cyano, hydroxyl, epoxy, silane, siloxane, alcohol, benzyl, carboxylate, ether, ether carboxylate, amidosulfonate, ether sulfonate, ester sulfonate, and urethane; and

at least one of R^8 and R^9, R^9 and R^{10}, and R^{10} and R^{11} together form an alkenylene chain completing a 5 or 6-membered aromatic ring, which ring may optionally include one or more divalent nitrogen, sulfur, selenium, tellurium, or oxygen atoms.

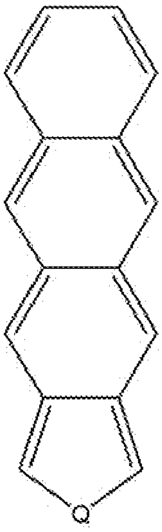
In some embodiments, the fused polycyclic heteroaromatic monomer has a formula selected from the group consisting of Formula V(a), V(b), V(c), V(d), V(e), V(f), V(g), V(h), V(i), V(j), and V(k):



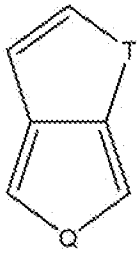
(Va)



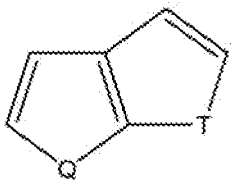
(Vb)



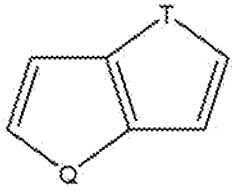
(Vc)



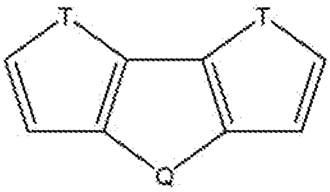
(Vd)



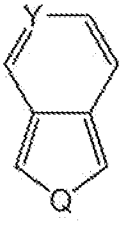
(Ve)



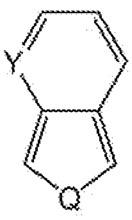
(Vf)



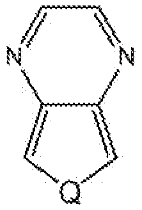
(Vg)



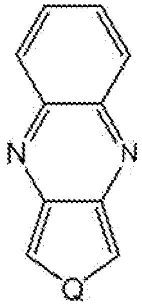
(Vh)



(Vi)



(Vj)



(Vk)

wherein:

Q is S, Se, Te, or NH; and

T is the same or different at each occurrence and is selected from S, NR^6, O, SiR^6_2, Se, Te, and PR^6;

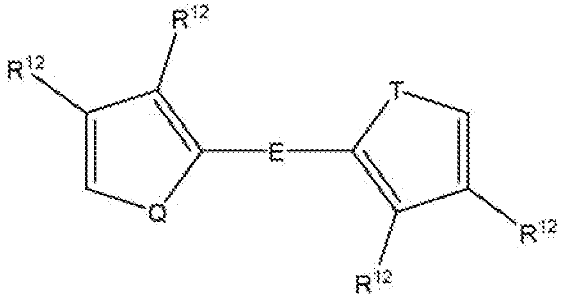
Y is N; and

R^6 is hydrogen or alkyl.

The fused polycyclic heteroaromatic monomers may be further substituted with groups selected from alkyl, heteroalkyl, alcohol, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, ester sulfonate, and urethane. In some embodiments, the substituent groups are fluorinated. In some embodiments, the substituent groups are fully fluorinated.

In some embodiments, the fused polycyclic heteroaromatic monomer is a thieno(thiophene). Such compounds have been discussed in, for example, Macromolecules, 34, 5746-5747 (2001); and Macromolecules, 35, 7281-7286 (2002). In some embodiments, the thieno(thiophene) is selected from thieno(2,3-b)thiophene, thieno(3,2-b)thiophene, and thieno(3,4-b)thiophene. In some embodiments, the thieno(thiophene) monomer is further substituted with at least one group selected from alkyl, heteroalkyl, alcohol, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, ester sulfonate, and urethane. In some embodiments, the substituent groups are fluorinated. In some embodiments, the substituent groups are fully fluorinated.

In some embodiments, polycyclic heteroaromatic monomers contemplated for use to form the polymer in the new composition comprise Formula VI:



(VI)

wherein:

Q is S, Se, Te, or NR^6;

T is selected from S, NR^6, O, SiR$^6_2$, Se, Te, and PR^6;

E is selected from alkenylene, arylene, and heteroarylene;

R^6 is hydrogen or alkyl;

R^{12} is the same or different at each occurrence and is selected from hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkythio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, aryl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, nitrile, cyano, hydroxyl, epoxy, silane, siloxane, alcohol, benzyl, carboxylate, ether, ether carboxylate, amidosulfonate, ether sulfonate, ester sulfonate, and urethane; or both R^{12} groups together may form an alkylene or alkenylene chain completing a 3, 4, 5, 6, or 7-membered aromatic or alicyclic ring, which ring may optionally include one or more divalent nitrogen, sulfur, selenium, tellurium, or oxygen atoms.

In some embodiments, the electrically conductive polymer is a copolymer of a precursor monomer and at least one second monomer. Any type of second monomer can be used, so long as it does not detrimentally affect the desired properties of the copolymer. In some embodiments, the second monomer comprises no more than 50% of the polymer, based on the total number of monomer units. In some embodiments, the second monomer comprises no more than 30%, based on the total number of monomer units. In some embodiments, the second monomer comprises no more than 10%, based on the total number of monomer units.

Exemplary types of second monomers include, but are not limited to, alkenyl, alkynyl, arylene, and heteroarylene. Examples of second monomers include, but are not limited to, fluorene, oxadiazole, thiadiazole, benzothiadiazole, phenylenevinylene, phenyleneethynylene, pyridine, diazines, and triazines, all of which may be further substituted.

In some embodiments, the copolymers are made by first forming an intermediate precursor monomer having the structure A-B-C, where A and C represent precursor monomers, which can be the same or different, and B represents a second monomer. The A-B-C intermediate precursor monomer can be prepared using standard synthetic organic techniques, such as Yamamoto, Stille, Grignard metathesis, Suzuki, and Negishi couplings. The copolymer is then formed by oxidative polymerization of the intermediate precursor monomer alone, or with one or more additional precursor monomers.

In some embodiments, the electrically conductive polymer is selected from the group consisting of a polythiophene, a polypyrrole, a polymeric fused polycyclic heteroaromatic, a copolymer thereof, and combinations thereof.

In some embodiments, the electrically conductive polymer is selected from the group consisting of poly(3,4-ethylenedioxythiophene), unsubstituted polypyrrole, poly(thieno(2,3-b)thiophene), poly(thieno(3,2-b)thiophene), and poly(thieno(3,4-b)thiophene).

3. Highly-fluorinated Acid Polymer

The highly-fluorinated acid polymer ("HFAP") can be any polymer which is highly-fluorinated and has acidic groups with acidic protons. The acidic groups supply an ionizable proton. In some embodiments, the acidic proton has a pKa of less than 3. In some embodiments, the acidic proton has a pKa of less than 0. In some embodiments, the acidic proton has a pKa of less than -5. The acidic group can be attached directly to the polymer backbone, or it can be attached to side chains on the polymer backbone. Examples of acidic groups include, but are not limited to, carboxylic acid groups, sulfonic acid groups, sulfonimide groups, phosphoric acid groups, phosphonic acid groups, and combinations thereof. The acidic groups can all be the same, or the polymer may have more than one type of acidic group. In some embodiments, the acidic groups are selected from the group consisting of sulfonic acid groups, sulfonamide groups, and combinations thereof.

In some embodiments, the HFAP is at least 95% fluorinated; in some embodiments, fully-fluorinated.

In some embodiments, the HFAP is water-soluble. In some embodiments, the HFAP is dispersible in water. In some embodiments, the HFAP is organic solvent wettable. The term "organic solvent wettable" refers to a material which, when formed into a film, possesses a contact angle no greater than 60°C with organic solvents. . In some embodiments, wettable materials form films which are wettable by phenylhexane with a contact angle no greater than 55°. The methods for measuring contact angles are well known. In some embodiments, the wettable material can be made from a polymeric acid that, by itself is non-wettable, but with selective additives it can be made wettable.

Examples of suitable polymeric backbones include, but are not limited to, polyolefins, polyacrylates, polymethacrylates, polyimides, polyamides, polyaramids, polyacrylamides, polystyrenes, and copolymers thereof, all of which are highly-fluorinated; in some embodiments, fully-fluorinated.

In one embodiment, the acidic groups are sulfonic acid groups or sulfonimide groups. A sulfonimide group has the formula:

$-SO_2-NH-SO_2-R$

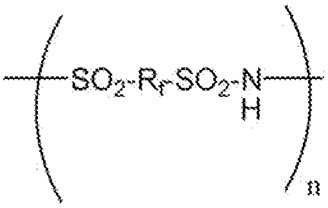
where R is an alkyl group.

In one embodiment, the acidic groups are on a fluorinated side chain. In one embodiment, the fluorinated side chains are selected from alkyl groups, alkoxy groups, amido groups, ether groups, and combinations thereof, all of which are fully fluorinated.

In one embodiment, the HFAP has a highly-fluorinated olefin backbone, with pendant highly-fluorinated alkyl sulfonate, highly-fluorinated ether sulfonate, highly-fluorinated ester sulfonate, or highly-fluorinated ether sulfonimide groups. In one embodiment, the HFAP is a perfluoroolefin having perfluoro-ether-sulfonic acid side chains. In one embodiment, the polymer is a copolymer of 1,1-difluoroethylene and 2-(1,1-difluoro-2-(trifluoromethyl)allyloxy)-1,1,2,2-tetrafluoroethanesulfonic acid. In one embodiment, the polymer is a copolymer of ethylene and 2-(2-(1,2,2-trifluorovinyloxy)-1,1,2,3,3,3-hexafluoropropoxy)-1,1,2,2-tetrafluoroethanesulfonic acid. These copolymers can be made as the corresponding sulfonyl fluoride polymer and then can be converted to the sulfonic acid form.

In one embodiment, the HFAP is homopolymer or copolymer of a fluorinated and partially sulfonated poly(arylene ether sulfone). The copolymer can be a block copolymer.

In one embodiment, the HFAP is a sulfonimide polymer having Formula IX:



$$\left(-SO_2-R_f-SO_2-\underset{H}{N}- \right)_n$$

(IX)

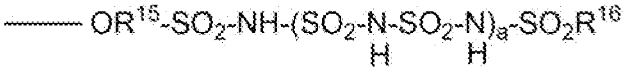
where:

R_f is selected from highly-fluorinated alkylene, highly-fluorinated heteroalkylene, highly-fluorinated arylene, and highly-fluorinated heteroarylene, which may be substituted with one or more ether oxygens; and

n is at least 4.

In one embodiment of Formula IX, R_f is a perfluoroalkyl group. In one embodiment, R_f is a perfluorobutyl group. In one embodiment, R_f contains ether oxygens. In one embodiment n is greater than 10.

In one embodiment, the HFAP comprises a highly-fluorinated polymer backbone and a side chain having Formula X:



$$-OR^{15}-SO_2-NH-(SO_2-\underset{H}{N}-SO_2-\underset{H}{N})_a-SO_2R^{16}$$

(X)

where:

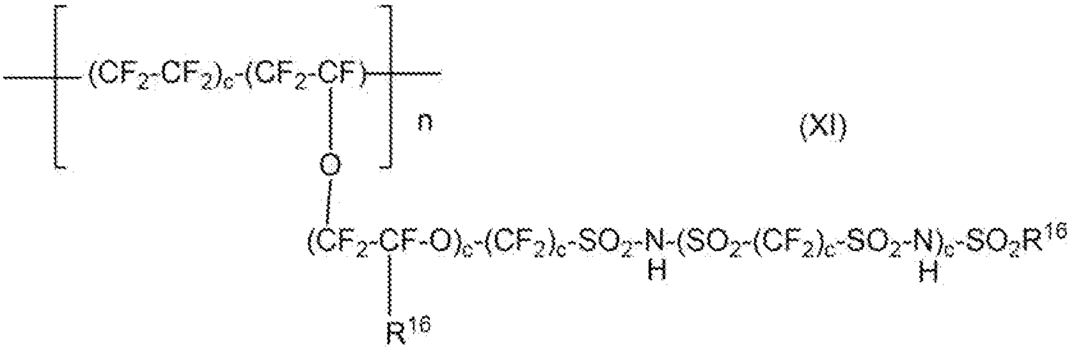
R^{15} is a highly-fluorinated alkylene group or a highly-fluorinated heteroalkylene group;

R^{16} is a highly-fluorinated alkyl or a highly-fluorinated aryl group;

and

a is 0 or an integer from 1 to 4.

In one embodiment, the HFAP has Formula XI:



$$-\left[(CF_2\text{-}CF_2)_c\text{-}(CF_2\text{-}\underset{\substack{|\\ O\\ |\\ (CF_2\text{-}\underset{\substack{|\\ R^{16}}}{CF}\text{-}O)_c\text{-}(CF_2)_c\text{-}SO_2\text{-}\underset{H}{N}\text{-}(SO_2\text{-}(CF_2)_c\text{-}SO_2\text{-}\underset{H}{N})_c\text{-}SO_2R^{16}}}{CF})\right]_n- \qquad \text{(XI)}$$

where:

R^{16} is a highly-fluorinated alkyl or a highly-fluorinated aryl group;

c is independently 0 or an integer from 1 to 3; and

n is at least 4.

The synthesis of HFAPs has been described in, for example, A. Feiring et al., J. Fluorine Chemistry 2000, 105, 129-135; A. Feiring et al., Macromolecules 2000, 33, 9262-9271; D. D. Desmarteau, J. Fluorine Chem. 1995, 72, 203-208; A. J. Appleby et al., J. Electrochem. Soc. 1993, 140(1), 109-111; and Desmarteau, U.S. Patent 5,463,005.

In one embodiment, the HFAP also comprises a repeat unit derived from at least one highly-fluorinated ethylenically unsaturated compound. The perfluoroolefin comprises 2 to 20 carbon atoms. Representative perfluoroolefins include, but are not limited to, tetrafluoroethylene, hexafluoropropylene, perfluoro-(2,2-dimethyl-1,3-dioxole), perfluoro-(2-methylene-4-methyl-1,3-dioxolane), $CF_2=CFO(CF_2)_tCF=CF_2$, where t is 1 or 2, and $R_f''OCF=CF_2$ wherein R_f'' is a saturated perfluoroalkyl group of from 1 to about ten carbon atoms. In one embodiment, the comonomer is tetrafluoroethylene.

In one embodiment, the HFAP is a colloid-forming polymeric acid. As used herein, the term "colloid-forming" refers to materials which are insoluble in water, and form colloids when dispersed into an aqueous medium. The colloid-forming polymeric acids typically have a molecular weight in the range of about 10,000 to about 4,000,000. In one embodiment, the polymeric acids have a molecular weight of about 100,000 to about 2,000,000. Colloid particle size typically ranges from 2 nanometers (nm) to about 140 nm. In one embodiment, the colloids have a particle size of 2 nm to about 30 nm. Any highly-fluorinated colloid-forming polymeric material having acidic protons can be used.
Some of the polymers described hereinabove may be formed in non-acid form, e.g., as salts, esters, or sulfonyl fluorides. They will be converted to the acid form for the preparation of conductive compositions, described below.

In some embodiments, HFAP include a highly-fluorinated carbon backbone and side chains represented by the formula

$-(O-CF_2CFR_f^3)_a-O-CF_2CFR_f^4SO_3E^5$

wherein R_f^3 and R_f^4 are independently selected from F, Cl or a highly-fluorinated alkyl group having 1 to 10 carbon atoms, a = 0, 1 or 2, and E^5. In some cases E^5 can be a cation such as Li, Na, or K, and be converted to the acid form.

In some embodiments, the HFAP can be the polymers disclosed in U.S. Patent No. 3,282,875 and in U.S. Patent Nos. 4,358,545 and 4,940,525. In some embodiments, the HFAP comprises a perfluorocarbon backbone and the side chain represented by the formula

$-O-CF_2CF(CF_3)-O-CF_2CF_2SO_3E^5$

where E^5 is as defined above. HFAPs of this type are disclosed in U.S. Patent No. 3,282,875 and can be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether $CF_2=CF-O-CF_2CF(CF_3)-O-CF_2CF_2SO_2F$, perfluoro(3,6-dioxa-4-methyl-7-octenesulfonyl fluoride) (PDMOF), followed by conversion to sulfonate groups by hydrolysis of the sulfonyl fluoride groups and ion exchanged as necessary to convert them to the desired ionic form. An example of a polymer of the type disclosed in U.S. Patent Nos. 4,358,545 and 4,940,525 has the side chain -O-$CF_2CF_2SO_3E^5$, wherein E^5 is as defined above. This polymer can be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether CF_2=CF-O-$CF_2CF_2SO_2F$, perfluoro(3-oxa-4-pentenesulfonyl fluoride) (POPF), followed by hydrolysis and further ion exchange as necessary.

One type of HFAP is available commericially as aqueous Nafion® dispersions, from E. I. du Pont de Nemours and Company (Wilmington, DE).

4. Inorganic Nanoparticles

The inorganic nanoparticles can be insulative or semiconductive.

In some embodiments, the inorganic nanoparticles are metal sulfides or metal oxides.

Examples of semiconductive metal oxides include, but are not limited to mixed valence metal oxides, such as zinc antimonates, and non-stoichiometric metal oxides, such as oxygen deficient molybdenum trioxide, vanadium pentoxide, and the like. Zinc antimonates, ZnO/Sb_2O_5, are commercially available from Nissan Chemical Company under the trade name "Celnax" in a variety of ratios (see, for example, US Patent 5,707,552).

Examples of insulative metal oxides include, but are not limited to, silicon oxide, titanium oxides, zirconium oxide, molybdenum trioxide, vanadium oxide, aluminum oxide, zinc oxide, samarium oxide, yttrium oxide, cesium oxide, cupric oxide, stannic oxide, antimony oxide, and the like.

Examples of metal sulfides include cadmium sulfide, copper sulfide, lead sulfide, mercury sulfide, indium sulfide, silver sulfide, cobalt sulfide, nickel sulfide, and molybdenum sulfide. Mixed metal sulfides such as Ni/Cd sulfides, Co/Cd sulfides, Cd/In sulfides, and Pd-Co-Pd sulfides may be used.

In some embodiments, the metal nanoparticles may contain both sulfur and oxygen. In some embodiments, combinations of metal nanoparticles are used.

Metal oxide nanoparticles can be made by reactive sputtering of metal in the presence of oxygen, evaporation of selected oxide, and multi-component oxides, or by vapor-phase hydrolysis of inorganic compounds, for example silicon tetrachloride. It can also be produced by sol-gel chemistry using hydrolyzable metal compounds, particularly alkoxides of various elements, to react with either by hydrolysis and polycondensation to form multi-component and multi-dimensional network oxides.

Metal sulfide nanoparticles can be obtained by various chemical and physical methods. Some examples of physical methods are vapor deposition, lithographic processes and molecular beam epitaxy (MBE) of metal sulfides such as cadmium sulfide, (CdS), lead sulfide (PbS), zinc sulfide (ZnS), silver sulfide (Ag_2S), molybdenum sulfide (MoS_2) etc. Chemical methods for the preparation of metal sulfide nanoparticles are based on the reaction of metal ions in solution either with H_2S gas or Na_2S in aqueous medium.

In some embodiments, the nano-particles are surface-treated with a coupling agent to be compatible with the aqueous electrically conducting polymers. The class of surface modifiers includes, but not limited to silanes, titanates, zirconates, aluminate and polymeric dispersant. The surface modifiers contain chemical functionality, examples of which include, but are not limited, to nitrile, amino, cyano, alkyl amino, alkyl, aryl, alkenyl, alkoxy, aryloxy, sulfonic acid, acrylic acid, phosphoric acid, and alkali salts of the above acids, acrylate, sulfonates, amidosulfonate, ether, ether sulfonate, estersulfonate, alkylthio, and arylthio. In one embodiment, the chemical functionality may include a crosslinker such as epoxy, alkylvinyl and arylvinyl group to react with the the conducting polymer in the nano-composite or hole-transporting material on the next upper layer. In one embodiment, the surface modifiers are fluorinated, or pefluorinated, such as tetrafluoro-ethyltrifluoro-vinyl-ether triethoxysilane, perfluorobutane-triethoxysilane, perfluorooctyltriethoxysilane, bis(trifluoropropyl)-tetramethyldisilazane, and bis (3-triethoxysilyl)propyl tetrasulfide.

5. Preparation of the Doped Electrically Conductive Polymer Compositions

In the following discussion, the conductive polymer, HFAP, and inorganic nanoparticles will be referred to in the singular. However, it is understood that more than one of any or all of these may be used.

The new electrically conductive polymer composition is prepared by first forming the doped conductive polymer and then adding the inorganic nanoparticles.

The doped electrically conductive polymer is formed by oxidative polymerization of the precursor monomer in the presence of the HFAP in an aqueous medium. The polymerization has been described in published U.S. patent applications 2004/0102577, 2004/0127637, and 2005/205860.

The inorganic nanoparticles can be added to the doped conductive polymer dispersion directly as a solid. In some embodiments, the inorganic nanoparticles are dispersed in an aqueous solution, and this dispersion is mixed with the doped conductive polymer dispersion. The weight ratio of nanoparticles to electrically conductive polymer is in the range of 0.1 to 10.0.

In some embodiments, the pH is increased either prior to the addition of the inorganic particles or after. The dispersions of doped conductive polymer and inorganic nanoparticles remain stable from the as-formed pH of about 2, to neutral pH. The pH can be adjusted by treatment with cation exchange resins prior to nanoparticle addition. In some embodiments, the pH is adjusted by the addition of aqueous base solution. Cations for the base can be, but are not limited to, alkali metal, alkaline earth metal, ammonium, and alkylammonium. In some embodiments, alkali metal is preferred over alkaline earth metal cations.

Films made from the new conductive composition described herein, are hereinafter referred to as "the new films described herein". The films can be made using any liquid deposition technique, including continuous and discontinuous techniques. Continuous deposition techniques, include but are not limited to, spin coating, gravure coating, curtain coating, dip coating, slot-die coating, spray coating, and continuous nozzle coating. Discontinuous deposition techniques include, but are not limited to, ink jet printing, gravure printing, and screen printing.

The films thus formed are smooth, relatively transparent, have a refractive index greater than 1.4 (@460nm wavelength), and can have a conductivity in the range of 10^{-7} to 10^{-3} S/cm.

6. Buffer Layers

In another embodiment of the invention, there are provided buffer layers deposited from aqueous dispersions comprising the new conductive polymer composition. The term "buffer layer" or "buffer material" is intended to mean electrically conductive or semiconductive materials and may have one or more functions in an organic electronic device, including but not limited to, planarization of the underlying layer, charge transport and/or charge injection properties, scavenging of impurities such as oxygen or metal ions, and other aspects to facilitate or to improve the performance of the organic electronic device. The term "layer" is used interchangeably with the term "film" and refers to a coating covering a desired area. The term is not limited by size. The area can be as large as an entire device or as small as a specific functional area such as the actual visual display, or as small as a single sub-pixel. Layers and films can be formed by any conventional deposition technique, including vapor deposition, liquid deposition (continuous and discontinuous techniques), and thermal transfer. Continuous deposition techniques, inlcude but are not limited to, spin coating, gravure coating, curtain coating, dip coating, slot-die coating, spray coating, and continuous nozzle coating. Discontinuous deposition techniques include, but are not limited to, ink jet printing, gravure printing, and screen printing.

The dried films of the new conductive polymer composition are generally not redispersible in water. Thus the buffer layer can be applied as multiple thin layers. In addition, the buffer layer can be overcoated with a layer of different water-soluble or water-dispersible material without being damaged.

Buffer layers comprising the new conductive polymer composition have been surprisingly found to have improved wettability. In some embodiments, films made from the new conductive polymer composition exhibit a contact angle with organic solvents of less than 50°. In some embodiments, the films are wettable with p-xylene with a contact angle less than 50°; in some embodiments, less than 40°; in some embodiments, less than 30°.

In another embodiment, there are provided buffer layers deposited from aqueous dispersions comprising the new conductive polymer composition blended with other water soluble or dispersible materials. Examples of types of materials which can be added include, but are not limited to polymers, dyes, coating aids, organic and inorganic conductive inks and pastes, charge transport materials, crosslinking agents, and combinations thereof. The other water soluble or dispersible materials can be simple molecules or polymers. Examples of suitable polymers include, but are not limited to, conductive polymers such as polythiophenes, polyanilines, polypyrroles, polyacetylenes, poly(thienothiophenes), and combinations thereof.

7. Electronic Devices

In another embodiment of the invention, there are provided electronic devices comprising at least one electroactive layer positioned between two electrical contact layers, wherein the device further includes the new buffer layer. The term "electroactive" when referring to a layer or material is intended to mean a layer or material that exhibits electronic or electro-radiative properties. An electroactive layer material may emit radiation or exhibit a change in concentration of electron-hole pairs when receiving radiation.

As shown in FIG. 1, a typical device, 100, has an anode layer 110, a buffer layer 120, an electroactive layer 130, and a cathode layer 150. Adjacent to the cathode layer 150 is an optional electron-injection/transport layer 140.

The device may include a support or substrate (not shown) that can be adjacent to the anode layer 110 or the cathode layer 150. Most frequently, the support is adjacent to the anode layer 110. The support can be flexible or rigid, organic or inorganic. Examples of support materials include, but are not limited to, glass, ceramic, metal, and plastic films.

The anode layer 110 is an electrode that is more efficient for injecting holes compared to the cathode layer 150. The anode can include materials containing a metal, mixed metal, alloy, metal oxide or mixed oxide. Suitable materials include the mixed oxides of the Group 2 elements (i.e., Be, Mg, Ca, Sr, Ba, Ra), the Group 11 elements, the elements in Groups 4, 5, and 6, and the Group 8-10 transition elements. If the anode layer 110 is to be light transmitting, mixed oxides of Groups 12, 13 and 14 elements, such as indium-tin-oxide, may be used. As used herein, the phrase "mixed oxide" refers to oxides having two or more different cations selected from the Group 2 elements or the Groups 12, 13, or 14 elements. Some non-limiting, specific examples of materials for anode layer 110 include, but are not limited to, indium-tin-oxide ("ITO"), indium-zinc-oxide, aluminum-tin-oxide, gold, silver, copper, and nickel. The anode may also comprise an organic material, especially a conducting polymer such as polyaniline, including exemplary materials as described in "Flexible light-emitting diodes made from soluble conducting polymer," Nature vol. 357, pp 477 479 (11 June 1992). At least one of the anode and cathode should be at least partially transparent to allow the generated light to be observed.

The anode layer 110 may be formed by a chemical or physical vapor deposition process or spin-cast process. Chemical vapor deposition may be performed as a plasma-enhanced chemical vapor deposition ("PECVD") or metal organic chemical vapor deposition ("MOCVD"). Physical vapor deposition can include all forms of sputtering, including ion beam sputtering, as well as e-beam evaporation and resistance evaporation. Specific forms of physical vapor deposition include rf magnetron sputtering and inductively-coupled plasma physical vapor deposition ("IMP-PVD"). These deposition techniques are well known within the semiconductor fabrication arts.

In one embodiment, the anode layer 110 is patterned during a lithographic operation. The pattern may vary as desired. The layers can be formed in a pattern by, for example, positioning a patterned mask or resist on the first flexible composite barrier structure prior to applying the first electrical contact layer material. Alternatively, the layers can be applied as an overall layer (also called blanket deposit) and subsequently patterned using, for example, a patterned resist layer and wet chemical or dry etching techniques. Other processes for patterning that are well known in the art can also be used.

The buffer layer 120 comprises the new conductive composition described herein. Buffer layers made from conductive polymers doped with HFAPs, generally are not wettable by organic solvents and have a refractive index below 1.4 (@460nm wavelength). The buffer layers described herein can be more wettable and thus are more easily coated with the next layer from a non-polar organic solvent. The buffer layers described herein also can have a refractive index greater than 1.4 (@460nm). The buffer layer is usually deposited onto substrates using a variety of techniques well-known to those skilled in the art. Typical deposition techniques, as discussed above, include vapor deposition, liquid deposition (continuous and discontinuous techniques), and thermal transfer.

An optional layer, not shown, may be present between the buffer layer 120 and the electroactive layer 130. This layer may comprise hole transport materials. Examples of hole transport materials have been summarized for example, in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 18, p. 837-860, 1996, by Y. Wang. Both hole transporting molecules and polymers can be used. Commonly used hole transporting molecules include, but are not limited to: 4,4',4"-tris(N,N-diphenyl-amino)-triphenylamine (TDATA); 4,4',4"-tris(N-3-methylphenyl-N-phenyl-amino)-triphenylamine (MTDATA); N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD); 1,1-bis[(di-4-tolylamino) phenyl]cyclohexane (TAPC); N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl)biphenyl]-4,4'-diamine (ETPD); tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-phenylenediamine (PDA); α-phenyl-4-N,N-diphenylaminostyrene (TPS); p-(diethylamino)benzaldehyde diphenylhydrazone (DEH); triphenylamine (TPA); bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP); 1-phenyl-3-[p-(diethylamino)styryl]-5-[p-(diethylamino)phenyl] pyrazoline (PPR or DEASP); 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane (DCZB); N,N,N',N'-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TTB); N,N'-bis(naphthalen-1-yl)-N,N'-bis-(phenyl)benzidine (α-NPB); and porphyrinic compounds, such as copper phthalocyanine. Commonly used hole transporting polymers include, but are not limited to, polyvinylcarbazole, (phenylmethyl)polysilane, poly(dioxythiophenes), polyanilines, and polypyrroles. It is also possible to obtain hole transporting polymers by doping hole transporting molecules such as those mentioned above into polymers such as polystyrene and polycarbonate.

Depending upon the application of the device, the electroactive layer 130 can be a light-emitting layer that is activated by an applied voltage (such as in a light-emitting diode or light-emitting electrochemical cell), a layer of material that responds to radiant energy and generates a signal with or without an applied bias voltage (such as in a photodetector). In one embodiment, the electroactive material is an organic electroluminescent ("EL") material. Any EL material can be used in the devices, including, but not limited to, small molecule organic fluorescent compounds, fluorescent and phosphorescent metal complexes, conjugated polymers, and mixtures thereof. Examples of fluorescent compounds include, but are not limited to, pyrene, perylene, rubrene, coumarin, derivatives thereof, and mixtures thereof. Examples of metal complexes include, but are not limited to, metal chelated oxinoid compounds, such as tris(8-hydroxyquinolato)aluminum (Alq3); cyclometalated iridium and platinum electroluminescent compounds, such as complexes of iridium with phenylpyridine, phenylquinoline, or phenylpyrimidine ligands as disclosed in Petrov et al., U.S. Patent 6,670,645 and Published PCT Applications WO 03/063555 and WO 2004/016710, and organometallic complexes described in, for example, Published PCT Applications WO 03/008424, WO 03/091688, and WO 03/040257, and mixtures thereof. Electroluminescent emissive layers comprising a charge carrying host material and a metal complex have been described by Thompson et al., in U.S. Patent 6,303,238, and by Burrows and Thompson in published PCT applications WO 00/70655 and WO 01/41512. Examples of conjugated polymers include, but are not limited to poly(phenylenevinylenes), polyfluorenes, poly(spirobifluorenes), polythiophenes, poly(p-phenylenes), copolymers thereof, and mixtures thereof.

Optional layer 140 can function both to facilitate electron injection/transport, and can also serve as a confinement layer to prevent quenching reactions at layer interfaces. More specifically, layer 140 may promote electron mobility and reduce the likelihood of a quenching reaction if layers 130 and 150 would otherwise be in direct contact. Examples of materials for optional layer 140 include, but are not limited to, metal chelated oxinoid compounds, such as bis(2-methyl-8-quinolinolato)(para-phenyl-phenolato)aluminum(III) (BAlQ) and tris(8-hydroxyquinolato)aluminum (Alq_3); tetrakis(8-hydroxyquinolinato)zirconium; azole compounds such as 2-(4-biphenylyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (PBD), 3-(4-biphenylyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole (TAZ), and 1,3,5-tri(phenyl-2-benzimidazole)benzene (TPBI); quinoxaline derivatives such as 2,3-bis(4-fluorophenyl)quinoxaline; phenanthroline derivatives such as 9,10-diphenylphenanthroline (DPA) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (DDPA); and any one or more combinations thereof. Alternatively, optional layer 140 may be inorganic and comprise BaO, LiF, Li_2O, or the like.

The cathode layer 150 is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode layer 150 can be any metal or nonmetal having a lower work function than the first electrical contact layer (in this case, the anode layer 110). As used herein, the term "lower work function" is intended to mean a material having a work function no greater than about 4.4 eV. As used herein, "higher work function" is intended to mean a material having a work function of at least approximately 4.4 eV.

Materials for the cathode layer can be selected from alkali metals of Group 1 (e.g., Li, Na, K, Rb, Cs,), the Group 2 metals (e.g., Mg, Ca, Ba, or the like), the Group 12 metals, the lanthanides (e.g., Ce, Sm, Eu, or the like), and the actinides (e.g., Th, U, or the like). Materials such as aluminum, indium, yttrium, and combinations thereof, may also be used. Specific non-limiting examples of materials for the cathode layer 150 include, but are not limited to, barium, lithium, cerium, cesium, europium, rubidium, yttrium, magnesium, samarium, and alloys and combinations thereof.

The cathode layer 150 is usually formed by a chemical or physical vapor deposition process. In some embodiments, the cathode layer will be patterned, as discussed above in reference to the anode layer 110.

Other layers in the device can be made of any materials which are known to be useful in such layers upon consideration of the function to be served by such layers.

In some embodiments, an encapsulation layer (not shown) is deposited over the contact layer 150 to prevent entry of undesirable components, such as water and oxygen, into the device 100. Such components can have a deleterious effect on the organic layer 130. In one embodiment, the encapsulation layer is a barrier layer or film. In one embodiment, the encapsulation layer is a glass lid.

Though not depicted, it is understood that the device 100 may comprise additional layers. Other layers that are known in the art or otherwise may be used. In addition, any of the above-described layers may comprise two or more sub-layers or may form a laminar structure. Alternatively, some or all of anode layer 110 the hole transport layer 120, the electron transport layer 140, cathode layer 150, and other layers may be treated, especially surface treated, to increase charge carrier transport efficiency or other physical properties of the devices. The choice of materials for each of the component layers is preferably determined by balancing the goals of providing a device with high device efficiency with device operational lifetime considerations, fabrication time and complexity factors and other considerations appreciated by persons skilled in the art. It will be appreciated that determining optimal components, component configurations, and compositional identities would be routine to those of ordinary skill of in the art.

In one embodiment, the different layers have the following range of thicknesses: anode 110, 500-5000 Å, in one embodiment 1000-2000Å; buffer layer 120, 50-2000 Å, in one embodiment 200-1000 Å; photoactive layer 130, 10-2000 Å, in one embodiment 100-1000 Å; optional electron transport layer 140, 50-2000 Å, in one embodiment 100-1000 Å; cathode 150, 200-10000 Å, in one embodiment 300-5000 Å. The location of the electron-hole recombination zone in the device, and thus the emission spectrum of the device, can be affected by the relative thickness of each layer. Thus the thickness of the electron-transport layer should be chosen so that the electron-hole recombination zone is in the light-emitting layer. The desired ratio of layer thicknesses will depend on the exact nature of the materials used.

In operation, a voltage from an appropriate power supply (not depicted) is applied to the device 100. Current therefore passes across the layers of the device 100. Electrons enter the organic polymer layer, releasing photons. In some OLEDs, called active matrix OLED displays, individual deposits of photoactive organic films may be independently excited by the passage of current, leading to individual pixels of light emission. In some OLEDs, called passive matrix OLED displays, deposits of photoactive organic films may be excited by rows and columns of electrical contact layers.

Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

It is to be appreciated that certain features of the invention which are, for clarity, described above and below in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination. Further, reference to values stated in ranges include each and every value within that range.

EXAMPLES

Comparative Example A

This comparative example illustrates low electrical conductivity and non-wettability of PAni/Nafion®, poly(tetrafluoroethylene)/ perfluoroethersulfonic acid, films, without added inorganic nanoparticles.

A PAni/Nafion® dispersion used in this example was prepared using an aqueous Nafion® colloidal dispersion having an EW (acid equivalent weight) of 1000. The Nafion® dispersion at 25% (w/w) was made using a procedure similar to the procedure in U.S. Patent No. 6,150,426, Example 1, Part 2, except that the temperature was approximately 270°C and was then diluted with water to form a 12.0% (w/w) dispersion for the polymerization.

In a 500mL reaction kettle were put 96.4g of 12% solid content aqueous Nafion® dispersion (11.57mmol SO_3H groups), 103g water. The diluted Nafion® was stirred at 300 RPM using an overhead stirrer fitted with a double stage propeller blade. To the diluted Nafion® dispersion, 1.21g (5.09mmol) sodium persulfate ($Na_2S_2O_8$) dissolved in 15mL water, and 422microL(4.63mmol) aniline dissolved in 266microL (9.28mmol) HCl and 20mL water were added rapidly. The polymerization liquid turned opaque and very viscous, but there was no visible change color in 5 minutes. ~20mg of ferric sulfate was added, but there was no visible change. However, the polymerization liquid started to turn bluish after 30 minutes and changed to green color thereafter. After about 8hrs, 25g of each *Dowex M31, and* Dowex M43 ion exchange resins, and 100g deionized water were added to the polymerization mixture. The mixture was stirred overnight and then filtered with a filter paper. The filtrate was added with 100g deionized water to reduce the viscosity. It was divided into five equal portions.

One portion was kept as-is without addition of a base. This portion was determined to have pH of 2, and contain 2.88% (w/w) PAni/Nafion®. Thin films were prepared from the PAni/Nafion® and subsequently baked at 130^{0}C in air. Room temperature electrical conductivity of the thin films was determined to be 1.2×10^{-8}S/cm, which is also shown in Table 1. One small drop of toluene was placed on one piece of thin film, but the toluene quickly rolled off the film, which indicates that the film surface was not wettable with a non-polar organic solvent. Non-polar solvent is commonly used for light emitting polymers and light-emitting small molecules.

The second portion of pH2 PAni/Nafion® was added with 0.1M NaOH water solution to pH5.0. This portion of Na^+ containing dispersion was determined to contain 2.89% (w/w) PAni/Nafion®. Electrical conductivity of thin films made from the pH5.0 PAni/Nafion® was determined to be 3.8×10^{-6}S/cm, which is also shown in Table 1. The PAni/Nafion® thin film was tested to be non-wettable with toluene.

Example 1

This example illustrates effect of semiconductive nano-particles on enhancement of electrical conductivity and wettability of PAni/Nafion®, poly(tetrafluoroethylene)/ perfluoroethersulfonic acid, films.

The pH2 and pH5.0 PAni/Nafion® dispersions prepared in Comparative Example 1 were used to illustrate embodiments of this disclosure. 5.0166g pH2 PAni/Nafion® dispersion was added with 1.1313g Celnax CX-Z300H-F2® (An aqueous zinc antimonite dispersion from Nissan Chemical Industries, Ltd. Houston, Texas, USA). CX-Z300H-F2 has pH of about 7 and contains 26.47% (w/w) zinc antimonite particles, which are less than 20nm in size. The weight ratio of PAni/Nafion® polymer to zinc antimonite in the formulation is about 0.47. The mixture forms a stable dispersion with no sign of sedimentation of particles over a period at least five months. It also forms smooth, transparent films upon drying of water. The data clearly illustrates that the particular tin antimonite particles from Celnax CX-Z300H-F2® are compatible with the PAni/ Nafion®. However, the process is to be improved by a more energy-intense process other than simply adding the two components together for improving surface smoothness having roughness less than at least 5nm. Thin film conductivity of the dispersion containing PAni/Nafion® and zinc antimonite was determined to be 6.6×10^{-4}S/cm (average of two film samples) at room temperature, which is also shown in Table 1. Conductivity was enhanced by more than four order magnitude. A piece of thin film was contacted with one drop of toluene. The toluene spread the film surface easily, which shows that the film becomes wettable with a common non-polar organic solvent.

pH5.0 PAni/Nafion® was also added with CX-Z300H-F2 to determine its effect on conductivity and wettability. 5.0666g pH5.0 PAni/Nafion® dispersion was added with 1.1450g Celnax CX-Z300H-F2®. The weight ratio of PAni/Nafion® polymer to zinc antimonite in the formulation is about 0.47. The mixture forms a stable dispersion with no sign of sedimentation of particles. It also forms smooth, transparent films upon drying of water. The data clearly illustrates that the particular tin antimonite particles from Celnax CX-Z300H-F2® are compatible with the PAni/ Nafion®. However, the process is to be improved by a more energy-intense process other than simply adding the two components together for improving surface smoothness having roughness less than at least 5nm. Thin film conductivity of the dispersion containing PAni/Nafion® and zinc antimonite was determined to be $9.3x10^{-4}$S/cm (average of two film samples) at room temperature, which is also shown in Table 1. Conductivity was enhanced by more than four order magnitude. A piece of thin film was contacted with one drop of toluene. The toluene spread the film surface easily, which shows that it becomes wettable with a common non-polar organic solvent.

Table 1
Effect of CX-Z300H-F2 on Electrical Conductivity

Dispersion pH and cation before addition of CX-Z300H-F2	Electrical conductivity (S/cm)	
	Without CX-Z300H-F2	With CX-Z300H-F2

$2.0/H^+$	$1.2x10^{-8}$	$6.6x10^{-4}$
$5.0/Na^+$	$3.8x10^{-8}$	$9.3x10^{-4}$

Example 2

This example illustrates preparation of an aqueous dispersion of polypyrrole (PPy) made in the presence of an aqueous dispersion of a copolymer of TFE (tetrafluoroethylene) and PSEPVE (perfluorinated 3,6-dioxa-4-methyl-7-octenesulfonic acid), a perfluorinated polymeric acid. This aqueous dispersion of PPy/ poly(TFE-PSEPVE) is used to illustrate effect of silica nanoparticles on wettability of PPYpoly(TFE-PSEPVE) solid film with organic solvents. An aqueous dispersion of poly(TFE-PSEPVE) was prepared by heating poly(TFE-PSEPVE) having EW of 1000 in water to ~270°C. The aqueous poly(TFE-PSEPVE) dispersion had 25%(w/w) poly(TFE-PSEPVE) in water and was diluted to 10.8% with deionized water prior to the use for polymerization with pyrrole.

Pyrrole monomer was polymerized in the presence of the poly(TFE-PSEPVE) dispersion as described in published U.S. patent application 2005-0205860. The polymerization ingredients have the following mole ratios: poly(TFE-PSEPVE):Pyrrole = 3.4; $Na_2S_2O_8$:pyrrole = 1.0; $Fe_2(SO_4)_3$:pyrrole = 0.1. The reaction was allowed to proceed for 15 minutes.

The aqueous PPy/poly(TFE-PSEPVE) dispersion was then pumped through three columns connected in series. The three columns contain Dowex M-31, Dowex M-43, and Dowex M-31 Na^+, respectively. The three Dowex ion-exchange resins are from Dow Chemicals Company, Midland, Michigan, USA. The ion-resin treated dispersion was subsequently microfluidized with one pass at 5,000psi using a Microfluidizer Processor M-110Y (Microfluidics, Massachusetts, USA). The microfluidized dispersion was then filtered and degassed to remove oxygen. The pH of the dispersion was measured to be 4.0 using a standard pH meter and solid% was determined to be 6.4% by a gravimetric method. Films spin-coated from the dispersion and then baked at 130°C in air for 10 minutes has a conductivity of 7.5×10^{-4} S/cm at room temperature.

The aqueous PPy/poly(TFE-PSEPVE) dispersion was first diluted from 6.4% to 3.12% before used for addition of silica nanoparticles. The silica naoparticle dispersion used in this example is IPA(isopropanol)-ST-S from Nissan Chemical Company. The IPA-ST-S contains 26w.% silica nanoparticle. Particle size of the silica was measured with a Microtrac "nano-ultra" dynamic light scattering. It was found that 50 volume% of the silica had particle size of 7.1nm(nanometer) or less. The silica dispersion was then mixed with a corresponding amount of PPy/poly(TFE-PSEPVE) dispersion to have desired silica w.% with respect to total solid, being PPy/poly(TFE-PSEPVE) and silica, which is listed in Table 2. The data clearly shows that contact angle of PPy/poly(TFE-PSEPVE) solid film formed by spin-coating drops drastically either with p-xylene or with anisole as silica is included.

Table 2

Effect of Silica on wettability of Polypyrrole(PPy)/poly(TFE-PSEPVE)

<u>Samples</u> (silica w.% of total solid)	Contact angle (degree)	
	P-xylene	Anisole
PPy/poly(TFE-PSEPVE) (0% silica)	50	55
PPy/poly(TFE-PSEPVE) (5.6% silica)	40	51

PPy/poly(TFE-PSEPVE) (10.5% silica)	29	42
PPy/poly(TFE-PSEPVE) (15.0% silica)	22	38
PPy/poly(TFE-PSEPVE) (20.0% silica)	19	31
PPy/poly(TFE-PSEPVE) (25.0% silica)	18	31

Example 3

This example illustrates the device performance of solution-processed organic light emitting diodes of a blue emitter using PPy/poly(TFE-PSEPVE) with and without silica as a buffer layer.

The PPy/poly(TFE-PSEPVE) dispersion with and without silica from Example 2 was used to form a buffer layer by spin-coating on patterned ITO substrates (device active area = 2.24 mm x 2.5 mm). The ITO substrates were cleaned and treated in a UV-zone oven for 10 minutes before use. Spin-coating of each PPy/poly(TFE-PSEPVE) dispersion with and without silica was set at conditions to provide thickness of 50nm after baked in air at 140°C for 7 minutes. They were then transferred to a dry box, in which all further top coating were conducted in an inert chamber. The buffer layer was then top-coated with a 0.38% (w/v) toluene solution of HT-2, which is an arylamine-containing copolymer having hole transport properties, to achieve 20nm thickness after baked at 275°C for 30mins in argon. After cooling, the substrates were spin-coated with an emissive layer solution containing 13:1 fluorescent host: blue fluorescent dopant, and subsequently heated at 135°C for 15 minutes to remove solvent. The layer thickness was approximately 40nm. The substrates were then masked and placed in a vacuum chamber. A 10nm thick layer of metal quinolate derivative as electron transporting layer was deposited by thermal evaporation, followed by a 0.8nm layer of cesium fluoride, and 100nm aluminum cathode layer. The devices were encapsulated using a glass lid, getter pack, and UV curable epoxy. The light emitting diode samples were characterized by measuring their (1) current-voltage (I-V) curves, (2) electroluminescence radiance versus voltage, and (3) electroluminescence spectra versus voltage. All three measurements were performed at the same time and controlled by a computer. The current efficiency (cd/A) of the device at a certain voltage is determined by dividing the electroluminescence radiance of the LED by the current density needed to run the device. The power efficiency (Lm/W) is the current efficiency divided by the operating voltage. The results are shown in Table 3, which illustrates that silica doesn't negatively affect device performance.

Table 3. Solution processed blue emitter using PPY/poly(TFE-PSEPVE) with and without silica as a buffer layer.

Device buffer layer material	Current Efficiency (cd/A)	Quantum efficiency (%)	CIEY	V (volt)	T50(h) @display luminance
PPy/poly(TFE-PSEPVE) (0% silica) #1 device	5.1	5.3	0.1145	4.84	17217 h @513 nits
PPy/poly(TFE-PSEPVE) (0% silica) #2 device	4.8	5.1	0.1100	4.44	18782 h @490 nits
PPy/poly(TFE-PSEPVE) (10.5% silica) #1 device	5.2	5.3	0.1163	4.51	23160 h @523 nits
PPy/poly(TFE-PSEPVE) (10.5% silica) #2 device	5.2	5.3	0.1138	4.52	22255 h @510 nits

PPy/poly(TFE-PSEPVE) (20.0% silica) #1 device	4.8	5.0	0.1094	4.56	21536 h @487 nits
PPy/poly(TFE-PSEPVE) (20.0% silica) #2 device	4.7	5.0	0.1098	4.46	20465 h @489 nits
PPy/poly(TFE-PSEPVE) (25.0% silica) #1 device	4.8	5.0	0.1123	4.68	20606 h @502 nits
PPy/poly(TFE-PSEPVE) (25.0% silica) #2 device	5.0	5.2	0.1138	4.66	22208 h @510 nits

All data @ 1000 nits unless noted; CIEY = y color coordinate according to the C.I.E. chromaticity scale (Commision Internationale de L'Eclairage, 1931); T50(h) = time to half luminance in hours @ 24°C.

Note that not all of the activities described above in the general description or the examples are required, that a portion of a specific activity may not be required, and that one or more further activities may be performed in addition to those described. Still further, the order in which activities are listed are not necessarily the order in which they are performed.

In the foregoing specification, the concepts have been described with reference to specific embodiments. However, one of ordinary skill in the art appreciates that various modifications and changes can be made without departing from the scope of the invention as set forth in the claims below. Accordingly, the specification and figures are to be regarded in an illustrative rather than a restrictive sense, and all such modifications are intended to be included within the scope of invention.

Benefits, other advantages, and solutions to problems have been described above with regard to specific embodiments. However, the benefits, advantages, solutions to problems, and any feature(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential feature of any or all the claims.

It is to be appreciated that certain features are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination.

The use of numerical values in the various ranges specified herein is stated as approximations as though the minimum and maximum values within the stated ranges were both being preceded by the word "about." In this manner slight variations above and below the stated ranges can be used to achieve substantially the same results as values within the ranges. Also, the disclosure of these ranges is intended as a continuous range including every value between the minimum and maximum average values including fractional values that can result when some of components of one value are mixed with those of different value. Moreover, when broader and narrower ranges are disclosed, it is within the contemplation of this invention to match a minimum value from one range with a maximum value from another range and vice versa.

CLAIMS

What is claimed is:

1. A composition comprising:

an aqueous disperson of at least one electrically conductive polymer doped with at least one highly fluorinated acid polymer, and

inorganic nanoparticles.

2. The composition of Claim 1, wherein the electrically conductive polymer is selected from the group consisting of polythiophenes, poly(selenophenes), poly(tellurophenes), polypyrroles, polyanilines, polycyclic aromatic polymers, copolymers thereof, and combinations thereof.

3. The composition of Claim 2, wherein the electrically conductive polymer is selected from the group consisting of a polyaniline, polythiophene, a polypyrrole, a polymeric fused polycyclic heteroaromatic, copolymers thereof, and combinations thereof.

4. The composition of Claim 3, wherein the electrically conductive polymer is selected from the group consisting of unsubstituted polyaniline, poly(3,4-ethylenedioxythiophene), unsubstituted polypyrrole, poly(thieno(2,3-b)thiophene), poly(thieno(3,2-b)thiophene), and poly(thieno(3,4-b)thiophene).

5. The composition of Claim 1, wherein the highly-fluorinated acid polymer is at least 95% fluorinated.

6. The composition of Claim 1, wherein the highly-fluorinated acid polymer is selected from a sulfonic acid and a sulfonimide.

7. The composition of Claim 1, wherein the highly-fluorinated acid polymer is a perfluoroolefin having perfluoro-ether-sulfonic acid side chains.

8. The composition of Claim 1, wherein the highly-fluorinated acid polymer is selected from the group consisting of a copolymer of 1,1-difluoroethylene and 2-(1,1-difluoro-2-(trifluoromethyl)allyloxy)-1,1,2,2-tetrafluoroethanesulfonic acid and a copolymer of ethylene and 2-(2-(1,2,2-trifluorovinyloxy)-1,1,2,3,3,3-hexafluoropropoxy)-1,1,2,2-tetrafluoroethanesulfonic acid.

9. The composition of Claim 1, wherein the highly-fluorinated acid polymer is selected from a copolymer of tetrafluoroethylene and perfluoro(3,6-dioxa-4-methyl-7-octenesulfonic acid), and a copolymer of tetrafluoroethylene and perfluoro(3-oxa-4-pentenesulfonic acid).

10. The composition of Claim 1, wherein the inorganic nanoparticles are semiconductive.

11. The composition of Claim 10, wherein in nanoparticles are selected from the group consisting of metal sulfides, metal oxides, and combinations thereof.

12. The composition of Claim 11, wherein the metal oxide is selected from the group consisting of zinc antimonates, indium tin oxide, oxygen-deficient molybdenum trioxide, vanadium pentoxide, and combinations thereof.

13. The composition of Claim 1, wherein the inorganic nanoparticles are insulative.

14. The composition of Claim 13, wherein the nanoparticles are selected from the group consisting of silicon oxide, titanium oxides, zirconium oxide, molybdenum trioxide, vanadium oxide, aluminum oxide,

zinc oxide, samarium oxide, yttrium oxide, cesium oxide, cupric oxide, stannic oxide, antimony oxide, and combinations thereof.

15. The composition of Claim 1, wherein the inorganic nanoparticles are selected from the group consisting of cadmium sulfide, copper sulfide, lead sulfide, mercury sulfide, indium sulfide, silver sulfide, cobalt sulfide, nickel sulfide, molybdenum sulfide, Ni/Cd sulfides, Co/Cd sulfides, Cd/In sulfides, Pd-Co-Pd sulfides, and combinations thereof.

16. The composition of Claim 1, wherein the weight ratio of nanoparticles to electrically conducting polymer is in the range of 0.1 to 10.0.

17. A film made from the composition of Claim 1.

18. The film of Claim 17 having a contact angle with p-xylene of less than 50°.

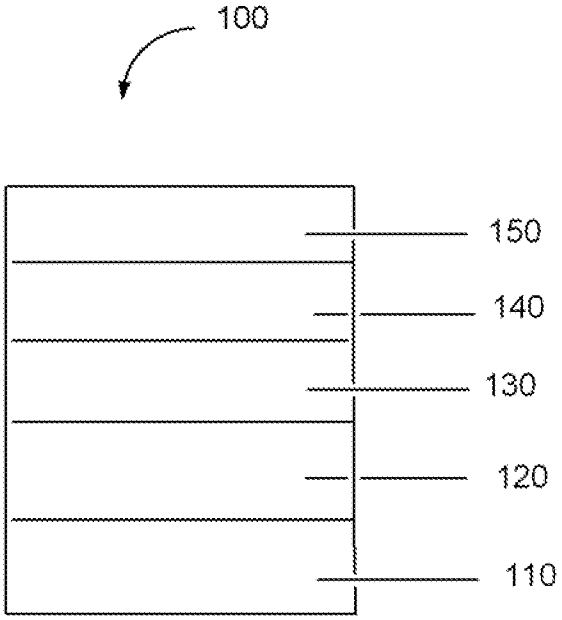
19 The film of Claim 17, having a refractive index greater than 1.4 at 460 nm.

20 An electronic device comprising at least one layer made from the composition of Claim 1.

21 The device of Claim 20, wherein the layer is a buffer layer.

22 The device of Claim 21, comprising an anode, a buffer layer, an electroactive layer, and a cathode.

FIGURE 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/35079

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01B 1/12 (2009.01)
USPC - 252/500

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)
IPC(8) - H01B 1/12 (2009.01)
USPC - 252/500

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 252/500 (keyword search)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST, WIPO, Web: Google, Google Scholar
Search Terms Used: layer, buffer, conductive polymer, highly fluorinated acid polymer, inorganic nanoparticle, aqueous dispersion, semiconducting, insulating, contact angle, electronic device, anode, cathode, electroactive layer, refractive index

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---------- Y	US 2006/0289843 A1 (Hsu et al.) 28 December 2006 (28.12.2006) Entire document, especially: Fig 2, abstract, para [0011]-[0013], [0019], [0021]-[0023], [0025], [0052], [0061], [0063], [0075], [0087]-[0090], [0092]-[0095], [0139], [0152], [0153], [0156], [0159], [0160], [0163], [0177], [0185]-[0188], [0190]-[0193], [0196], [0213], [0220], [0223], [0229], [0245], [0249], [0251]; Examples 1, 3, 4, 5, 6, 7;	1-12, 16-18, 20-22 -------------------------- 13-15, 19
Y	US 2002/0192476 A1 (Kambe et al.) 19 December 2002 (19.12.2002) Entire document, especially: Figs 19-25; para [0186], [0189]-[0193]	13, 14, 19
Y	US 7,112,369 B2 (Wang et al.) 26 September 2006 (26.09.2006) Entire document, especially: Examples 4, 6-8, 10	15
A	US 7,189,771 B2 (Hsu) 13 March 2007 (13.03.2007) Entire document	1-12, 16-18, 20-22

☐ Further documents are listed in the continuation of Box C. ☐

*	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 02 April 2009 (02.04.2009)	Date of mailing of the international search report 09 APR 2009
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774