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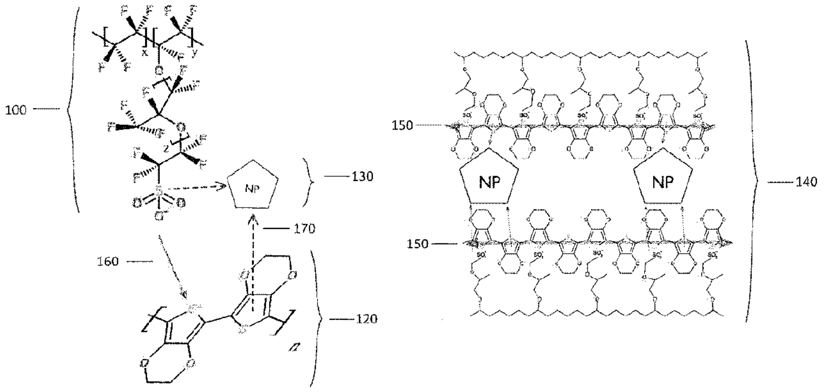

FIG.1

(57) Abstract: The present disclosure relates to conductive polymers referred to as nanocomposite conducting matrix (NCM). The present NCMs may be used, for example, in conductive coatings such as electromagnetic shielding or seed layer for electrochemical deposition, in ink-jet printing as a conductive ink for conventional and 3D printings, in wearable electronics, in electrochromic devices, in electronic interconnects and electronic devices such as organic and inorganic transistors and diodes, displays, organic and inorganic photovoltaics, organic and inorganic light emitting diodes, and as electrode material for energy storage devices like type-I and type-II batteries, super-capacitors and ultra- capacitors using semi-transparent conductive nanocomposite polymers, and the like.

CONDUCTING NANOCOMPOSITE MATRIX & USES THEREOF

FIELD

The present disclosure relates to conductive polymers referred to as nanocomposite conducting matrix (NCM).

BACKGROUND

Electrically conductive materials are the primary components in a variety of applications in energy, utilities industries, consumer electronics and related technology. Traditionally interconnects are made of films of transition metals. Noble metals such as copper (Cu), silver (Ag) and gold (Au), exhibit the best conductive properties. However, the conductivity advantage can be outweighed by the expense of the raw materials, complex and energy consuming processes such as physical vapour deposition and chemical etching, and the brittleness and likelihood of cracking upon bending. As an alternative to pure metallic materials, composite materials have been developed over the years. Silver epoxy [Aumiller et al., 1978] is a composite material composed of a sulphur bearing component (1) like a chloro-sulphonated polyethylene, a vinyl monomer (2) like methyl methacrylate, particles of conductive material (3) like micrometer size silver flakes, and a catalyst (4) like N,N-dimethylaniline. These alternatives tend to require less complex and expensive manufacturing processes such as screen printing which facilitate their integration into traditional and emerging technologies. However there are numerous limitations such as lack of transparency, incompatibility with ink-jet printing, and the poor or limited flexibility. Conductive organic materials have been discovered in the 50's, and their potential application in interconnect technology has only been explored in the early 80's [Diaz and Logan, 1980]. This trend ultimately led to the development of conjugated conducting polymer dispersions, for instance [Jonas and Krafft, 1991] used a mixture of polythiophene dispersions (1) like poly(3,4-ethylenedioxythiophene) (PEDOT) and a polyanions (2) like poly(styrenesulfonate) (PSS) in solution. The conductivity of this polymer can substantially be increased from 10^2 Ω.cm down to 10^{-4}Ω.cm [Ouyang and Xia, 2011] by using chemical treatments. However, the poor processability of this polymer makes it difficult to use with high throughput fabrication processes and applications.

Transparent conductive oxides (TCOs) are used in applications requiring transparency in the visible spectrum range [King and Veal, 2011]. For instance, liquid crystal displays, plasma displays, flat panel displays and touch panels use a TCO commonly known as indium tin oxide (ITO) which offers a best compromise between transparency (≥80%) and bulk resistivity ($10^{-4}\Omega$.cm). Even though ITO is used in various optical coatings such as infrared-reflecting coatings due to its high thermal stability (up to 1400°C), it requires, as with many other TCOs, complex deposition techniques.

TCO materials are typically deposited on substrates using chemical vapour deposition, magnetron sputtering, sublimation, or spray pyrolysis. These techniques require high temperature during either deposition or the post annealing step; a process that is energy intensive and can irreversibly damage certain substrates.

Flexibility, weight and safety are the primary considerations in efforts to incorporate TCOs on flexible substrate. In addition, it is desirable to offer alternatives to the rigid transparent substrates that are commonly used in electronic displays and touch panels. Low-cost organic electronic device like organic field effect transistors (OFETs), organic light emitting diodes (OLEDs) and organic photovoltaic cells (OPVs) rely heavily on TCOs such as ITO and aluminum-doped zinc oxide (AZO) to act as charge collectors due to their conductivity, good mobility, transparency and workfunction.

However, achieving the desired mechanical stability of TCOs on flexible substrates has been proven problematic. Alternatives to TCOs, such as thin metal sheets in OLEDs and OPVs [Krebs, 2009], have been proposed but these systems typically compromise on performance in terms of, for instance, transparency or weight. US7,985,490 describes organic electroluminescent devices. Fig. 1a of this reference illustrates an organic electroluminescent device having an emissive layer (12) formed on a first electrode (10), a hole injection or “buffer” layer (11) formed between the electrode and emissive layer, a hole barrier layer (13) formed on the emissive layer, and a second electrode (14) formed thereon. US7,317,047 describes electrically conducting organic polymer/nanoparticle composites which may contain a conductive organic polymer and a nanoparticle which may be either an inorganic or an organic nanoparticle.

It would be advantageous to provide conducting materials with one or more properties such as the ability to be tuneable, semi- or full-transparency, light weight, flexible, resistance to deformation, chemical resistance, water resistance, heat resistance, substrate-free, ease of processing, and cost effectiveness.

SUMMARY

The present disclosure provides in part a conductive and transparent polymer material. In certain embodiments the present material is compatible with current large-scale fabrication processes such as, but not limited to, screen printing, blading, spray coating, spin casting, paint brushing, slot die, jet printing, inkjet printing, 3D printing, embossing, molding, physical vapour deposition, chemical vapor deposition, electrochemical deposition, or the like. In certain embodiments the present material can be used in conductive substrates, conductive inks, conductive sheets, conductive foam, interconnects, anode and/or cathode, hole collectors/injectors, electron collectors/injectors, gate electrodes, electronic devices, electronic components, electronic displays, polymer electronics, photo-electronic devices, opto-electronic devices, electromagnetic devices and components, or the like.

The present NCMs may be used, for example, in conductive coatings such as electromagnetic shielding or seed layer for electrochemical deposition, in ink-jet printing as a conductive ink for conventional and 3D printings, in wearable electronics, in electrochromic devices, in electronic interconnects and electronic devices such as organic and inorganic transistors and diodes, displays, organic and inorganic photovoltaics, organic and inorganic light emitting diodes, and as electrode material for energy storage devices like type-I and type-II batteries, super-capacitors and ultra-capacitors using semi-transparent conductive nanocomposite polymers, and the like.

The present disclosure further provides a method of producing the present materials.

In one aspect, the present NCM relates to an electrically conducting, semi- or fully-transparent, membrane serving as a substrate, sheet, foam, shield, interconnect, anode and/or cathode, hole collector/injector, electron collector/injector, gate electrode, electronic displays, polymer electronics, and/or photo-electronic layer, etc. The present NCM may advantageously be thin, flexible and/or mechanically resistant.

In an embodiment, the NCM may comprise a perfluorosulfonic acid-PTFE copolymer (PSAP) with short side chains and a thiophene based polymer (PT). The PSAP may act as a structural matrix and an electron acceptor while the PT may act as an electron donor and semi-conductor backbone when the transport is taking place. The NCM may comprise additional electron donor polymers like poly(styrene sulfonic acid) (PSS), nano-particles of various metals like transition metals, post-transition metals, metalloids, alkali metals, alkaline earth metals, non-metals or a combination of the aforementioned elements. In metal oxides, this embodiment, physical properties such as electronic affinity, workfunction, conductivity, carrier type and mobility, or the optical transmission and absorption may be tuned.

The NCM may be transparent or semi-transparent in the visible range with a limited absorption of light between 400 nm to the near-infrared wavelength. NCM absorption in the visible and invisible range can be tuned, for example, by using nano-particles with specific absorption resonance, nano-structures exhibiting plasmonic resonances and/or materials with photonic gap such as photonic crystal fabricated using for example, but not limited to, embossing, stamping, laser interfering lithography, maskless lithography, stencil lithography, laser etching, focused ion beam (FIB) or electron beam lithography (EBL), for instance, or a combination of materials and techniques.

In certain embodiments the present NCM is superior in terms of mechanical strength and stability of the physical properties under adverse conditions such as moisture, temperature variations, or deformations.

The present disclosure provides a process for fabricating fully- and semi- transparent OLEDs and OPVs devices using the NCM as semi-transparent anodes and cathodes. In another aspect, the present disclosure provides NCMs for use in the fabrication of a fully- or semi-transparent thin electrode material for electronic displays such as, but not limited to, liquid crystal displays, plasma displays, flat panel displays, or the like. In another aspect, the present disclosure provides NCMs for use in the fabrication of conductive, fully- or semi-transparent thin electrode materials suitable for electronic and telecommunication components such as, but not limited to, 2D interconnects, 3D and/or stacked electronic interconnects, diodes, vertical interconnect access (VIAs), micro-strip antennas, electromagnetic shields and seed layer for electrochemical deposition, electrochromic devices, inorganic electronics, electrodes for energy storage devices like type-I and type-II batteries.

In certain embodiments, the present NCMs can show similar device performance to common transparent conductive coatings, while having an enhanced resistance to deformation and/or to adverse environmental conditions. In certain aspects, the present NCMs can be processed using standard techniques such as screen printing, blading, spray coating, spin casting, paint brushing, slot die, jet printing, inkjet printing, 3D printing, embossing, molding, physical vapour deposition, chemical vapor deposition, electrochemical deposition, or the like deposition. This may lower the overall cost associated with transparent conductive coatings such as transparent conducting oxides (TCOs).

As used herein, the term "nanocomposite conducting matrix" and "NCM" refers to an electrically conducting material comprising at least one electron donor substance, at least one electron acceptor substance, and at least one nanoparticle.

As used herein, the term "electron donor substance" refers to a polymer material that is energetically favourable in its cationic form to acting generally as a reducing agent. For example, the present electron donor substance may be poly(fluorine)s, polyphenylenes, polypyrenes, polyazulenes, polynaphthalenes, poly(acetylenes)s (PAC), poly(p-phenylene vinylene) (PPV), poly(pyrrole)s (PPY), polycarbazoles, polyindoles, polyazepines, polyanilines (PANI), or poly(thiophene)s (PT), or the like.

As used herein, the term "electron acceptor substance" refers to a polymer material that is energetically favourable in its anionic form to acting generally as an oxidizing agent. For example, the present electron acceptor substance may be sulfonated polycarbonates, polystyrene sulfonates, polyvinyl sulfonates, perfluorosulfonic acid polymers, perfluorosulfonic acid based copolymers, polystyrene carboxylates, polyvinyl carboxylates, perfluorocarboxylic acid polymers or perfluorocarboxylic acid based copolymers, or the like.

As used herein, the term "nanoparticle" refers to particles having a cross-sectional diameter of less than about 2000 nm, about 1000 nm, about 500 nm, about 250 nm, about 200 nm, about 150 nm, about 100 nm, about 50 nm, about 20 nm. The particles may be any suitable shape such as, for example, spherical, tubular, crystalline, or sheet-like.

This summary does not necessarily describe all features of the invention. Other aspects, features and advantages of the invention will be apparent to those of ordinary skill in the art upon review of the following description of specific embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** illustrates a proposed chemical structure of an embodiment of the present NCM.

FIG. **2** shows an SEM profile of an embodiment of the present NCM.

FIG. **3** shows transport, valence band and workfunction measurements of an NCM on a glass substrate with approximately 300 nm in thickness.

FIG. **4** shows the characterization of the mechanical properties, solvent resistance and heat resistance of one example of the present NCM with approximately 300nm in thickness sprayed on cellulose acetate film compared to a commercially available PET substrate with 100nm of ITO.

FIG. **5** shows designs and data characterizing the usage of two instances of the NCM in OPVs fully spray coated in air.

FIG. **6** shows designs and data characterizing the usage of the NCM in semi-conductor/metal hetero- junctions.

FIG. **7** shows designs and data characterizing the usage of an instance of the NCM in OLEDs sprayed and spin coated in air.

FIG. **8** shows SEM and transmission spectrum with and without the nano-hole array created using FIB on 500 nm of one instance of the NCM spray on a glass slide.

FIG. **9** shows a comparison of typical electro-optical films and those comprising the present NCMs.

FIG. **10** shows spray coated and doctor bladed NCM films, and a LED panel using NCM interconnects.

DETAILED DESCRIPTION

The present nanocomposite conducting matrix (NCM) comprises at least one electron donor substance, at least one electron acceptor substance, and at least one nanoparticle. The NCM is electrically conducting and preferably transparent or semi-transparent.

The present NCM may comprise any suitable electron donor substance. Examples of electron donor substances include, but are not limited to, poly(fluorine)s, polyphenylenes, polypyrenes, polyazulenes, polynaphthalenes, poly(acetylenes)s (PAC), poly(p-phenylene vinylene) (PPV), poly(pyrrole)s (PPY), polycarbazoles, polyindoles, polyazepines, polyanilines (PANI), poly(thiophene)s (PT), or combinations thereof. Preferred electron donor substances include, but are not limited to, poly(thiophene) polymers such as, for instance, poly(3,4-ethylenedioxythiophene) (PEDOT).

The present NCM may comprise any suitable amount of electron donor substance. For example, the present NCM may comprise about 0.1% or greater, about 0.5% or greater, about 1% or greater, about 1.5% or greater, about 2% or greater, about 2.5% or greater, about 3% or greater, about 3.5% or greater, about 4% or greater, about 4.5% or greater, about 5% or greater, by volume, of electron donor substance. The present NCM may comprise about 85% of less, about 80% of less, about 75% of less, about 70% of less, about 65% of less, about 60% of less, by volume, of electron donor substance.

The present NCM may comprise any suitable electron acceptor substance. Examples of electron acceptor substances include, but are not limited to, hydrogenated polymers, partially fluorinated polymers or perfluorinated polymers and/or copolymer comprising at least one carbonate and/or one sulfonate end-group like sulfonated polycarbonates, polystyrene sulfonates, polyvinyl sulfonates, perfluorosulfonic acid polymers or perfluorosulfonic acid based copolymers, polystyrene carboxylates, polyvinyl carboxylates, perfluorocarboxylic acid polymers, perfluorocarboxylic acid based copolymers, or combinations thereof. Preferred electron acceptor substances include, but are not limited to, perfluorosulfonic acid-PTFE copolymers like for instance XUS® (from Dow Chemicals, see [Zaluski et al. 1994]) or Aquivion®.

The electron acceptor may be a polymer with sulfur-containing side chains. For example, perfluorosulfone side chains. Preferably the polymer has short side chains such as four or fewer carbon atoms, such as, three or two carbon atoms. For example, the side chain may be a perfluorosulfone chain having three or two fluoro-substituted carbon atoms e.g. -O-CF2-CF2-SO_xH. While not wishing to be bound by theory, it is believed that the short side chain of the fluoropolymer backbone causes the NCM to be more resistant to deformation, become hydrophobic in its matrix form, and potentially more solvent/heat resistant. In certain embodiments the electron acceptor polymers have self assembly properties with the nanoparticles as shown in FIG. **1**.

The present NCM may comprise any suitable amount of electron acceptor substance. For example, the present NCM may comprise about 1% or greater, about 5% or greater, about 10% or greater, about 15% or greater, about 20% or greater, about 25% or greater, about 30% or greater, about 35% or greater, about 40% or greater, by volume, of electron donor substance. The present NCM may comprise about 85% of less, about 80% of less, about 75% of less, about 70% of less, about 65% of less, by volume, of electron donor substance.

The present NCM may comprise any suitable nanoparticle. For example, alkali metals, alkali earth metals, transition metals, post-transition metals, metal oxides, metalloids, non-metals nanoparticles, nanorods, nanosheets, nanocrystallites, or the like. Preferred elemental nanoparticles and/or oxide compounds include, but are not limited to, those comprising aluminium, zinc, magnesium, copper, indium, silicon, chromium, nickel, iron, cobalt, titanium, vanadium, strontium, cobalt, niobium, ruthenium, silver, palladium, platinum, gold, graphene, yttrium, barium, calcium, or suitable combinations thereof. Preferred nanoparticles include, but are not limited to silver, indium, gold, platinum, palladium, manganese, copper oxide, aluminum oxide, magnesium oxide, zinc oxide, titanium oxide, cobalt oxide, niobium oxide, europium oxide, activated carbon and graphene oxide, or suitable combinations thereof.

The nanoparticle may have any suitable diameter but preferred are those having a cross-sectional diameter of about 100 nm or less, about 80 nm or less, about 60 nm or less, about 40 nm or less, about 30 nm or less, about 20 nm or less, about 10 nm or less, about 5 nm or less. Preferred are nanoparticles having a diameter of about 1 nm or greater, about 2 nm or greater, about 3 nm or greater, about 4 nm or greater, about 5 nm or greater, about 6 nm or greater, about 7 nm or greater, about 8 nm or greater, about 9 nm or greater, about 10 nm or greater.

In certain embodiments, the nanocomposite conducting matrix according comprises at least one nanoparticle that comprises a metal ion, wherein the metal ion is selected from those having s-type electron sub-shell. In certain embodiments, the nanocomposite conducting matrix according comprises at least one nanoparticle that comprises a metal ion, wherein the metal ion is selected from those having a p-type, d-type, or f-type electron sub-shell. While not wishing to be bound by theory it is believed that metal ions having a s-type sub-shell provide NCMs with a higher workfunction while those with p-type, d-type, or f-type electron sub-shells provide a lower workfunction.

The present NCM may comprise any suitable amount of nanoparticles. For example, the present NCM may comprise about 0.1% or greater, about 0.5% or greater, about 1% or greater, about 1.5% or greater, about 2% or greater, about 2.5% or greater, about 3% or greater, about 3.5% or greater, about 4% or greater, about 4.5% or greater, about 5% or greater, about 6% or greater, about 7% or greater, about 8% or greater, about 9% or greater, about 10% or greater, by volume, of nanoparticles. The present NCM may comprise about 50% of less, comprise about 45% of less, comprise about 40% of less, comprise about 35% of less, comprise about 30% of less, by volume, of nanoparticles.

The specific type or combination of nanoparticle(s) used herein may enable various properties to be adjusted somewhat. For example, one or more of conductivity, carrier mobility, IR and UV absorption spectrum, workfunction, transparency, surface morphology and wettability, etc., may be adjustable.

In an exemplary embodiment, the present NCM comprises 63.9% by volume of sulfonated fluoropolymer Aquivion®, 9.00% by volume of thiophene based polymer poly(3,4-ethylenedioxythiophene) also known as PEDOT, 22.4% by volume of sulfonated polystyrene poly(styrene sulfonic acid) also known as PSS, and 4.77% by volume of indium nanoparticles having a diameter of about 20nm.

In an exemplary embodiment, the present NCM comprises 63.9% by volume of sulfonated fluoropolymer Aquivion®, 9.0% by volume of PEDOT, 22.4% by volume of sulfonated polystyrene poly(styrene sulfonic acid) also known as PSS, and 4.7% by volume of silver nanoparticles having a diameter of about 20nm.

In an exemplary embodiment, the present NCM comprises 63.9% by volume of sulfonated fluoropolymer Aquivion®, 9.0% by volume of PEDOT, 22.4% by volume of sulfonated polystyrene poly(styrene sulfonic acid) also known as PSS, and 4.7% by volume of palladium nanoparticles having a diameter of about 20nm.

In an exemplary embodiment, the present NCM comprises 63.9% by volume of sulfonated fluoropolymer Aquivion®, 9.0% by volume of PEDOT, 22.4% by volume of sulfonated polystyrene poly(styrene sulfonic acid) also known as PSS, and 4.7% by volume of platinum nanoparticles having a diameter of about 20nm.

In an exemplary embodiment, the present NCM comprises 63.9% by volume of sulfonated fluoropolymer Aquivion®, 9.0% by volume of PEDOT, 22.4% by volume of sulfonated polystyrene poly(styrene sulfonic acid) also known as PSS, and 4.7% by volume of gold nanoparticles having a diameter of about 20nm.

In an exemplary embodiment, the present NCM comprises 64.9% by volume of sulfonated fluoropolymer Aquivion®, 9.0% by volume of PEDOT, 22.4% by volume of sulfonated polystyrene poly(styrene sulfonic acid) also known as PSS, and 4.7% by volume of alumina nanoparticles having a diameter of about 20nm.

In an exemplary embodiment, the present NCM comprises 64.9% by volume of sulfonated fluoropolymer Aquivion®, 9.0% by volume of PEDOT, 22.4% by volume of sulfonated polystyrene poly(styrene sulfonic acid) also known as PSS, and 4.7% by volume of zinc oxide nanoparticles having a diameter of about 20nm.

In an exemplary embodiment, the present NCM comprises 64.9% by volume of sulfonated fluoropolymer Aquivion®, 9.0% by volume of PEDOT, 22.4% by volume of sulfonated polystyrene poly(styrene sulfonic acid) also known as PSS, and 4.7% by volume of magnesium oxide nanoparticles having a diameter of about 20nm.

In an exemplary embodiment, the present NCM comprises 64.9% by volume of sulfonated fluoropolymer Aquivion®, 9.0% by volume of PEDOT, 22.4% by volume of sulfonated polystyrene poly(styrene sulfonic acid) also known as PSS, and 4.7% by volume of activated carbon nanoparticles having a diameter of about 50 nm or less.

In an exemplary embodiment, the present NCM comprises 64.9% by volume of sulfonated fluoropolymer Aquivion®, 9.0% by volume of PEDOT, 22.4% by volume of sulfonated polystyrene poly(styrene sulfonic acid) also known as PSS, and 4.7% by volume of graphene oxide nanosheets having a thickness of about a monolayer and a length of about 1000 nm or less.

The present NCMs may be formed into films. For example, films having an average thickness of about 10cm or less, 1 cm or less, 1 mm or less, 100µm or less, 10 µm or less, 1000 nm or less, about 800 nm or less, about 600 nm or less, about 400 nm or less, about 200 nm or less. The present films may have an average thickness of about 20 nm or greater, about 40 nm or greater, about 60 nm or greater, about 80 nm or greater, about 100 nm or greater, about 1000 nm or greater, about 10 µm or greater.

As used herein, a “layer” of a given material includes a region of that material the thickness of which is less than either of its length or width. Examples of layers may include sheets, foils, films, laminations, coatings, blends of organic polymers, metal plating, and adhesion layer(s), for example. Further, a “layer” as used herein need not be planar, but may alternatively be folded, bent or otherwise contoured in at least one direction, for example.

A typical OPV will comprise a substrate such as glass or plastic with multiple layers thereon. These include, for example, an anode layer (TCO), a hole collector layer, a photo-active layer, an optional buffer layer, and a cathode layer. A typical OLED has a similar structure except the photo-active layer is replaced with a photo-emissive layer. The present NCMs offer the potential to replace these complex multilayer systems with a less complex assembly. Less layers in an assembly generally requires less manufacturing steps. The present disclosure provides a film assembly comprising (or consisting essentially of) a photo-active layer (e.g. an emissive layer or photosensitive layer), an anode collector assembly comprising NCM, and a cathode collector assembly comprising NCM. The present disclosure provides an electro-optical device comprising (or consisting essentially of) a substrate, an emissive layer, an anode collector assembly comprising NCM, and a cathode collector assembly comprising NCM. The present disclosure provides an electro-optical device comprising (or consisting essentially of) a substrate, a photosensitive layer, an anode collector assembly comprising NCM, and a cathode collector assembly comprising NCM.

The anode collector assembly comprising NCM may replace, for example, the substrate, the TCO, for instance ITO, with reasonably good transparency and conductivity. The anode assembly comprising NCM may replace, for example, the hole injection layer (HCL) or hole collector layer (HIL) conventionally fulfilled by the PEDOT:PSS layer. This may be achieved in using a low workfunction material, for instance, indium nanoparticles. The precise adjustment of the ratio of the nanoparticles may be used to match the workfunction of the NCM with the valence band of the active layer by reducing the Schottky barrier. Among other things, the number of optical interfaces is decreased, leading to an improvement of the light transmission through the device.

The cathode collector assembly comprising NCM may replace, for example, the metallic cathode and/or the hole blocking layer (HBL). The present cathode assembly offers the advantage of a stabilized pH over the whole device that can mitigate the cathode degradation induced by the active polymer acidity. By adapting the workfunction of the NCM with lower workfunction nanoparticles, for instance aluminium, the workfunction of the NCM may be tuned to match the bottom of the conduction band of the active layer.

The present devices using the NCM materials at the anode and cathode exhibit semi-transparency on both sides which may be useful when bi-directionality of light emission or absorption is necessary. Using metallic nanoparticles, the NCM workfunction range may be extended below the 5.2eV limit typically seen in PEDOT:PSS compositions, and render the films suitable for electronic devices such as optical devices (ODs), OLEDs, OPVs, etc. The present films may, for example, be used as anode, cathode and gate elements in OFETs. The present NCMs may have a workfunction of about 5.1eV or less, about 5.0eV or less, about 4.9eV or less, about 4.8eV or less, about 4.7eV or less, about 4.6eV or less, about 4.5eV or less, about 4.4eV or less, about 4.3eV or less, about 4.2eV or less, about 4.1eV or less, about 4.0eV or less, about 3.9eV or less, about 3.8eV or less, about 3.7eV or less, about 3.6eV or less, about 3.5eV or less, about 3.4eV or less, about 3.3eV or less, about 3.2eV or less, about 3.1eV or less, about 3.0eV or less.

The present films may, for example, be used as an anode collector in elements of electronic devices such as, for example, flexible displays. The films may partially or fully replace three components of an anode collector assembly substrate/ITO/PEDOT:PSS in electronic devices such as, for instance, OLEDs and OPVs.

The present films may, for example, be used as an anode collector and/or an electrode collector in elements of electrochromic devices such as, for example, electrochromic windows. The films may partially or fully replace ITO in electrochromic devices such as, for instance, electrochromic windows. The films may partially or fully replace two components of an anode collector assembly substrate/ITO and/or two components of a cathode collector assembly susbtrate/ITO in electrochromic devices such as, for instance, electrochromic windows. The films may partially or fully replace three components of an anode collector assembly substrate/ITO/buffer and/or two components of a cathode collector assembly susbtrate/ITO/buffer in electrochromic devices such as, for instance, electrochromic windows.

The present NCMs may be used as an ink in, for example, conventional printing, 3D printings, or wearable electronics.

The present films may, for example, be used as a cathode collector assembly in devices such as OLEDs and OPVs.

The present disclosure provides methods of manufacturing an electro-optical display comprising a substrate, a photoactive layer such as an emissive and/or photosensitive layer, an anode collector assembly comprising NCM, and a cathode collector assembly comprising NCM. The method may comprise providing a substrate, providing an anode coating composition comprising NCM, providing a cathode coating composition, providing a photoactive layer; applying to the substrate the anode coating, applying the photoactive layer to the anode coating, and applying cathode coating to the photoactive layer.

The present NCMs may, for example, be used as coating material for electromagnetic cavity, electrochemical deposition, defrosting coating, antistatic coating and electromagnetic shielding; as material or ink for electronic interconnects, conventional and 3D printing, wearable electronics, vertical inter-connect access, micro-strip antennas, organic and inorganic transistors and diodes, inorganic photovoltaics, and inorganic light emitting diodes; as a wire material used to make an ultralight and flexible coil to generate AC and DC magnetic fields; as a substrate or component for electrochromic devices such as electrochromic windows; or as a current collector material for energy storage devices like type-I and type-II batteries, super-capacitors and ultra-capacitors, or as combination of thereof.

The present NCMs can be processed in any suitable manner such as, for example, casting, blading, spraying, brush painting or printing in a variety of atmospheres. The present NCMs may be etched or engraved with, but not limited to, lasers, reactive ion etching (RIE), FIB milling, embossing, in a variety of atmospheres or under vacuum. The present NCMs may be ink impressed and stamped.

Ionomer polymers typically comprise repeat units of both electrically neutral repeating units and a fraction of ionized units. These polymers have interesting physicochemical properties. Common examples include PSS, PEDOT, and Nafion®. PSAP matrices such as XUS®, Aciplex®, Nafion® or Aquivion® are extensively used in fuel cells technology for their ionic transport capability and their micro-scale porosity. Moreover, these compounds are known to present superior mechanical and thermal stability. PEDOT is a conducting polymer having acceptable optical transparency (such as 10% of optical absorption in the visible spectrum), good stability, and moderate band gap (1.4 to 2.4eV) with low redox potential. However, PEDOT in its polymer form is insoluble in water making its large scale usage difficult. PEDOT in the binary copolymer form PEDOT:PSS is naturally water soluble; PSS was known and extensively used in medical applications but has found a new usage as a hole doping agent of PEDOT.

The conductive characteristics of PEDOT:PSS is known to be related to the interplay between the deprotonation of the sulfonyl groups that produce a hole charge transfer to the PEDOT chain and what is called a Peierl instability which is related to the PEDOT chain deformation caused by a local potential modification due to a charge transfer. PEDOT:PSS is a p-type semiconductor with a conductivity up to 600S/m and a transparency of about 80% in the UV light regime. However, a poor conductivity compared to TCO and the relatively high workfunction ($\approx$5.2eV) of PEDOT:PSS generally limit the usage of this material to the hole injector layer (HIL) and/or hole collector layer in organic electronic devices. Additionally, the strong acidic nature and hygroscopic properties of this binary mixture are considered as impediments to more widespread usage.

Attempts have been made to produce a more stable exhibiting better performance HIL material using binary mixtures essentially based on a ionomer with low water intake and a conducting polymer has been proposed and seems to show some improvement in terms of stability and efficiency in OLEDs but the workfunction is still in the high range (≥ 5.55eV) restricting the usage of these binary mixture as hole transport layer only.

In certain embodiments of the present NCMs the deprotonation properties of the side chain termination of a PSAP, such as Aquivion®, present a high density of very short and light side chains which carry the functional SO_xH group in conjunction with the proton acceptor susceptibility of a PT like PEDOT. It is believed that these composite polymers have self assembly properties with specific nanoparticles as shown in FIG. **1**. The constrained structure of the Aquivion® **100** (or XUS®) due to very short side chains ($z=0$) seems to be favourable to forming a strong cross link with the PT chain **120** and the nanoparticles **130**. This may protect the PT backbone and render the nanocomposite polymer network compact and homogeneous **140**. It is believed that atoms at the surface of the nanoparticles create organometallic bonds **170** which can modify the valence states in the PT chains and the PSAP, helping the charge transfer **160** and improving the conductivity in the conduction channels **150**. While not wishing to be bound by theory, it is believed that the short side chain of the fluoropolymer backbone causes the NCM to be more resistant to deformation, become hydrophobic in its matrix form, and more solvent/heat resistant.

Scanning electron microscopy (SEM) and FIB measurements of the NCM presented in FIG. **2** illustrate the structural difference between Aquivion® **230** and the NCM **210**. The two examples of NCM presented comprise a volume ratio of approximately 14:2:5:1 of Aquivion®:PEDOT:PSS:Ag-NPs (silver nanoparticles). The glass substrates **220** where first cleaned with acetone for 10 min, followed by an isopropyl alcohol (IPA) rinse and sonication for 10 min. The substrates were rinsed in deionized water and dried with nitrogen (N_2) gun. Polar solvents, for example 1-propanol and 2-propanol, may be added in specific proportion to the NCM formulation to increase its viscosity to 20cps in order to enable spray coating technique and achieve a film thickness of 500nm with a corrugation better than approximately 50nm. The spray coating equipment was thoroughly washed and decontaminated after every usage. The NCM formulation has been first spray coated using air flow through a shadow mask on a clean glass substrate or on an Aquivion® membrane preliminary cleaned with a solution of 1M sulfuric acid and then rinsed with DIW. The rate of deposition may be 300nm/min of solid material. The thickness of material was verified using a semiconductor grade profilometer. The coatings were allowed to dry in the air at 150°C for one hour before insertion in a vacuum. As used herein, NCMAg refers to the composite polymer modified with the metallic element silver. Other metallic elements may be substituted. The Aquivion® **230** possesses gaps that are typical of the aforementioned micro-porous structure in the family of PSAP, while the NCM **210** possesses a more compact structure with few or no gaps. This can also be observed after FIB milling onto the NCM, which is correlated with a high density polymer. Moreover, it should be noted that even though the surface presents some traces of impurity, possibly due to the use of an unfiltered NCM solution, it is relatively even and follows the glass substrate morphology.

The PSAP can be considered an acidic environment since the sulfonic acids are stronger acids than the corresponding carboxylic acids end-group. In the case of high density of side chains such as the short side chain PSAP Aquivion® or XUS®, one would expect a negative pKa which corresponds to having a low probability of having nanoparticles in their oxide form. As a consequence, most of the transition-metals, metalloids or post-transition metals will be in the cationic or metallic form at the surface of the nanoparticles within the polymer matrix.

In certain embodiments, the physical properties of the NCM can be tuned, for instance, by adjusting the acidity, by increasing the density of acidic end-groups in the polymer like sulfonyl or carboxyl hydroxide end-groups, and/or by adding other sulfonated or carboxylated polymers or impurities in the form of nanoparticles in their metallic or oxide form. Thermodynamically alkali metals, alkali earth metals, transition metals, post-transition metals or metalloids, tend to be in their cationic or metallic form in the acidic region of the stability phase diagram. For example, in the metallic phase indium has a workfunction of 4.1 eV while in its oxidized state (In_2O_3) the work function is 5.3-5.4 eV. If the indium is oxidized it must be reduced in, for example, an acid bath to obtain a lower workfunction. In addition, processing pure indium can be problematic. While not wishing to be bound by theory, it is believed that the present NCMs provide the 'acidic' environment so the workfunction can be set lower by holding the nanoparticle in its metallic form.

It certain embodiments, it may be possible to 'tune' the physical properties of the NCMs by using the tendency of metals to fully use their valence orbitals and consequently bridge with polyatomic ligand creating organometallic complexes. For instance, the modification of the local potential due to the proximity of a heavy nucleus with 4d valence orbitals in close proximity to the sulphur, carbon and oxygen sites on the TP and/or the PSAP has several consequences that are illustrated by the schematics **FIG.1** and the experimental data depicted in **FIG. 3**. Referring to **FIG. 3**, the XPS spectra of the level 2p of sulfur **330** and 1s of oxygen **340** give an indication of the changes happening at the nanoscale level in the structure with the presence of nanoparticles. The level S2p is a double peak structure with a ratio 2:1 because of the spin orbit coupling. This is a generic feature in the XPS spectrum for this energy level. For each double peak structure with this ratio corresponds a sulfur site in the NCM with its local potential. **330** present at minimum four discernable structures and in reality, it is probably more as the broadening of each peaks can hide multiple relevant features. The main broad feature showing a maximum at 168.5eV of binding energy (BE) has been identified to be the double peak of the ionized sulfonate site -[SO_3^-] with the asymmetry toward higher binding energy due an offset of the double feature of 0.4eV of the non ionized sulfonate site –[SO_3H] contribution. The other main feature already identified at 164.5eV of BE is to be related to the sulfur site on the PT chain. The ratio between the sulphonate sites and the thiophene sites is of the order of 9:1 which is correlated with the composition of our NCMs. Additionally, two more sharp double peaks structure exist on the thiophene energy range with one peak maxima at 165eV and another at 166eV. These are visible on all spectra and are an indication of two new chemical environments on the sulfur atom of PT chain which are promoted or repressed by the addition of nanoparticles; they probably correspond to the same crystalline configuration but with different oxidation states. The same sort of analysis can be done on the 1s level of oxygen. The data seem to show that the oxygen environment on the thiophene site and on the sulfonate sites –[SO_3H], most probably oxidation states, are anti-correlated and change function of the type of nanoparticles. These observation on **330** and **340** may indicate that if the chemical environment of the oxygen and sulfur sites, particularly the oxidation states, are modified, then the valence band and filling must be impacted as these sites are directly or indirectly involved in the conductive properties of the polymer. The valence band spectra and the workfunction are presented **320** and seem to confirm the link between the nanoparticle type and the level of alteration of the valence band and the filling level. When the nanoparticle are transition metals like silver or zinc, the band structure alteration is maximum due to the d-type valence shell with a maximum shift on the work function from -1.1±0.1eV for the NMCZn to -0.5±0.1eV for NCMIn compared to the NCMC with a work function of 5.1±0.1eV. When the nanoparticles are of sp-type valence shell, the delocalization seems to have less impact on the valence band of the system, generating only a small change on the work function with only a -0.2±0.1eV shift for NCMAl compared to NCMC. The work function shift seems to correlates with the vanishing of the S2p structure at 166eV. From the observed chemical shifts and new core level peaks of sulphur and oxygen compared to the reference polymer being PEDOT:PSS, it is believed that the new local potential due to the intrinsic composition of the NCM modified the valence band spectrum due to the formation of organometallic bonds at the surface of the nanoparticles with a mixed ionic-covalent nature. Consequently, the changes in the hybridization of the molecular orbitals appear in the valence band as new states have likely emerge as illustrated by the series of valence band measured by X-ray photoelectron spectroscopy (XPS) on several parts of the NCM. This can also leads to a modification of the density of state near the Fermi level, a change in the carrier mobility in the conduction channel, and potentially a change in the electronic affinity in the case of extreme perturbations. **330** illustrates the variation of sheet resistance measurements on a layer of various instances of the NCM of approximately of 500nm in thickness and spray coated in air on a glass substrate. A correlation between the simplest oxidation state of the nanoparticle and the conductivity seems to exist although this correlation is not perfect as the nature of the organometallic bonds between the nanoparticles and the PT chain and/or the PSAP are not purely ionic. These series of experiments show the possibility of a relative control over the electronic properties of the NCM using specific nanoparticles.

Three procedures have been used to monitor the resistivity of the NCM samples under various environmental stresses. The reference material used for these tests was a commercially available 100 nm ITO-coated on a 100 µm PET. NCMIn has been selected as NCM material because of a workfunction in the range of ITO, and it was deposited on EVA. EVA substrates where cleaned by immersion in isopropyl alcohol (IPA) and sonication for 10 min. The substrates were dipped in deionized water and then dried off with nitrogen (N_2) gun. Polar solvents, for example 1-propanol and 2-propanol, may be added in specific proportion to the NCMIn to increase its viscosity to 20cps and to allow the use of spray coating and meet a film thickness specification of 500nm with a corrugation better than 100nm. 1ml of NCMIn formulation has been first spray coated in air over a masked area of 3.0in by 3.0in on a clean EVA substrate at a rate of 300nm/min of solid material. The thickness of material was verified using a semiconductor grade profilometer. The EVA/NCMIn assembly was then cured at 80°C for 30min to get rid of most of the moisture. Rectangular strips of NCMIn and ITO of dimension 0.4in by 2.0in have been used as test samples. Referring now to **FIG. 4**, extreme deformations **410** have been applied using the following procedure. The resistivity of the samples was monitored from a flat configuration **412** to a DNA coil with stretch **414** by incrementally reducing the bending radius and returning to the initial flat configuration **412**. Considering the extreme fragility of ITO to mechanical stress, the bending has been applied inward in the case of the TCO sample, and in both orientations for the NCMIn sample. **410** shows an irreversible degradation of the resistivity of the ITO sample from 220Ω to 4kΩ, ; the degradation of ITO under bending and stretching reflects a known weakness of TCOs. The NCMIn sample was less sensitive to the applied deformation, the resistivity remaining unaltered at 1.4kΩ until the EVA substrate broke under an extreme stretch strain. It is notable that NCMIn has high a resistivity of 1.4kΩ. This may be associated with the poor surface quality of the EVA grade and the low curing temperature. The heat resistance **420** has been tracked by subjecting the samples to a flow of hot air at 400°C at 5cm of distance. The ITO sample show a clear transition when the PET start to deform under the effect of heat. The ITO sample irreversibly exhibits a resistivity increase of 4 orders of magnitude from 208Ω to 2.4MΩ even though the PET did not break. In the case of the NCMIn, the flow of the EVA happened faster but did not seem to change the capacity of the polymer to conduct the current. The resistivity increases linearly from 1.2kΩ to 1.8kΩ over 120s until the EVA melts, burns and breaks under the effect of the heat after 120s. The results **420** seem to indicate that NCM is weakly impacted by the temperature of the environment, even at the extreme level that causes substrate melting. The NCMIn solvation properties **430** have been tested using a polar protic solvent (deionized water) and a polar aprotic solvent (acetone). The procedure consisted of a series of complete immersion of the sample into solvent for 1min immediately followed by resistivity measurement. The initial measurement was done when the sample were dry, followed by soaking the sample in the acetone and subsequently deionized water, followed by drying in air without external assistance. The maximum change of resistivity happens after one minute in water where the resistivity almost doubled, going from 1.56kΩ to 3.4kΩ, but returned to 2.2kΩ upon drying. This partial degradation of the conductivity of the NCM after successively soaking the sample in polar protic and aprotic solvent for few minutes seems to be an indication of the incompatibility of the EVA substrate with acetone, which could cause the NCMIn to slightly delaminate from the substrate. ITO has been used as reference in this experiment even though it is know that this procedure does not change its physical properties. The NCM tested under deformation, heat and solvation stress shows little or no degradation. Existing conducting polymers are for the most part hydrophilic and present degradation issues upon contact with water.

The generation of Schottky barriers, ohmic barriers and metal to semiconductor heterojunctions is important in the manufacture of electronic devices. Two configurations of heterojunction using n-type semiconductor phenyl-C_{61}-butyric acid methyl ester (PCBM) are presented in **FIG. 6**. to illustrate the use of the NCM in the field of electronic devices. The first one **600** consists of a stack of PCBM **630** over NCMZn **620** on a top of a PET substrate **610.** The second device **601** consists of a stack of NCMAl **640** over PCBM **630** over NCMZn **620** on top of a PET substrate **610**. The devices where manufactured using a layer-by-layer spray coating technique. 100μm PET substrates **610** were first cleaned in acetone for 10 min, isopropyl alcohol (IPA), deionized water. The PET samples were dried using a nitrogen (N_2) gun. Polar solvents, for example 1-propanol and 2-propanol, may be added in specific proportion to the NCM formulations **620** and **630** to increase the viscosity to 20cps to be allow spray coating. This may be used to meet a film thickness specification of 1μm with a corrugation better than 50nm. **630** was prepared by dissolving 20 mg/ml of PCBM in 1,2,dichlorobenze (anhydrous) and stirred for approximately 12 hours at room temperature in air. The obtained PCBM solution is subsequently filtered with a 0.45 μm polypropylene (“PP”) syringe filter in order to remove any undissolved cluster. The spray coating equipment was thoroughly washed and decontaminated after every sequence of usage. For the device **600**, 1ml of NCMAl formulation has been first spray coated with high purity N_2 on a clean PET substrate through a a shadow masked of 1.0in by 0.5in at a rate of 300nm/min of solid material. The thickness of material was verified using a semiconductor grade profilometer. The PET/NCM assembly was then cured at 150°C for 30min to get rid of moisture. The PCBM solution was then immediately spray coated with dry high purity N_2 on a mask over the PET/NCM assembly on top of hot plate set at 80°C for 30 sec at a rate of 400nm/min. The final NCM/PCBM junction overlap over a region of 0.2in. For the device **601**, an additional step was added after the PCBM coating which is identical to the first layer of NCMZn with the exceptions of the shadow mask location and that the NCMZn/PCBM remained on top of the hot plate. In this case the NCMAl electrode was over a 200nm layer of PCBM. Great care was taken to avoid a short between the NCMZn electrode and the NCMAl electrode. 4-point contact measurements have been performed with using probe station in ambient environment. The current versus voltage (I-V)characteristic are disclosed in **604** for the device **600** and in **605** for the device **601**. **602** represents the electronic configuration of **600** for a contactless device where each layer is represented respective to the vacuum level. **603** represents the electronic configuration of **601** for a contactless device where each layer is represented respective to the vacuum level. For the device **600**, the I-V characteristic shows that the current flow in one direction is definitely favoured over the reverse bias, there is virtually no leakage of current until about 3.13V with a substantially low current of about 1μA. It can also be seen that the positive region does not have a very steep slope as expected in our case considering the fabrication process. Looking at the characteristic of the junction, we found a barrier voltage of 227±3mV, a current of 0.101±0.006μA, a resistance of 7.1±0.1kΩ and a forward voltage drop of 1.30±0.03V using the ideal diode equation with inclusion of the parasitic resistance. This is indicative of an built in series resistance that could be have multiple origins. Possibly the point contacts with the various materials, the junction between **620** and **630** or originating from the thickness of **630**. For the device **601**, the I-V curve is characteristic of an asymmetric metal/semiconductor/metal junction. As a matter of comparison, NCMX/NCMY junctions, where X and Y are two different types of metallic nanoparticles, are purely ohmic. The Schottky barrier signature of the device **600** and **601** demonstrates that the NCM materials can be used in electronic devices like diodes and field effect transistors, and also suggest that one could advantageously replace the complex TCO/PEDOT:PSS assembly by a unique layer of NCM in electronic devices

Charge collection at the collectors of OPV devices remains an issue. The polymer used can be strongly acidic and, since it is an electrochemical cell, this can be detrimental to conductive materials based on metal and metal oxides. For instance, PEDOT:PSS is known to have a pH<1 and under illumination, the anodic and cathodic potential as well as various environment conditions (e.g. illumination, temperature, moisture level, the oxygen concentration, etc.) can increase the electrochemical activity at the interfaces. ITO is known to be dissolved by PEDOT:PSS; under such conditions, this material is thermodynamically more stable in a cationic form opposed to the oxide form. The same applies to aluminium even under a cathodic potential in direct contact to the photo-active polymer blend. PEDOT:PSS can also experience instances of de-wetting from the ITO substrate and de-lamination from the photoactive polymer blend under adverse conditions such as heat. This is thought to be related to a thermal dilatation constant mismatch. Additionally, other instabilities against oxidation and reduction in the junction as well as the potential recrystallization of the photoactive polymer blend can lead to the device degradation and a rapid decay of the device performances.

The various issues described herein related to hetero-electrode configuration like for instance substrate/ITO/PEDOT:PSS configuration in the OPVs or OLEDs may also apply in the field of organic electronics where similar configurations of TCO/polymer are used. To be used as an alternative for the substrate/TCO/conductive polymer hetero-interface, the NCM preferably meets one or more of the following criteria: (a) a work function essentially identical and tunable over an identical range to current configurations, (b) an optimized barrier height and as close as possible to an Ohmic junction characteristic, (c) charge selectivity so current leakage is minimized in the case of usage with bulk heterojunction, (d) electrochemical and chemical stability under normal usage conditions, and (d) physical properties minimally affected by water with good mechanical properties.

Referring to **FIG. 5**, a conventional OPV **501** is composed of a transparent or semi-transparent carrier substrate **510** typically glass or polyethylene terephthalate (PET), an anode electrode **520** typically ITO **522**, a hole collector layer (HCL) **530** typically PEDOT:PSS, a photoactive polymer **540** typically poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM), an optional hole blocking layer **550** typically calcium, and an cathode electrode **560** typically aluminum **562**. The photoactive polymer may be made by dissolving 20 mg/ml of P3HT and 20 mg/ml of PCBM separately in 1,2,dichlorobenze (anhydrous) and stirring for approximately 12 hours at room temperature in air. The P3HT:PCBM (1:1) blend is then made by mixing the two 1,2, dichlorobenzene solutions, followed by stirring with a magnetic stirrer at 60 ^{o}C for approximately 72 hours in air. The obtained P3HT:PCBM active polymer solution is subsequently filtered with a 0.45 μm polypropylene (“PP”) syringe filter in order to remove any undissolved cluster. The Al cathode is usually deposited using physical vapor deposition at base pressure of 1 μTorr and deposition rate of 1.5 Ang/s. The flat band energy diagram **502** of a conventional OPV shows the process of exciton dissossiation at the interface of the electron donor polymer P3HT **542** and the electron acceptor PCBM **544**. One embodiment of the present NCM related to organic photovoltaics (OPVs) is shown in **FIG 5**. The anode assembly ITO/PEDOT:PSS (TCO/HCL) has been replaced by a spray coated layer of NCMIn **524**, which is semi-transparent and conductive with a workfunction similar to ITO **522**. The NCM comprises Aquivion®, PEDOT, PSS and indium oxide nanoparticles (average diameter of 20 nm) in a volume ratio of about 14:2:5:1. The diameter of the nanoparticle is chosen to be approximately 20 nm and the material is chosen so the workfunction of the NCM match the valence band of the photo-active layer**.** The aim is to reduce the probability of having a Schottky barrier, as illustrated in FIG. **6,** and improving hole collection. In one embodiment, the total thickness of the NCM is about 100-1000 nm, preferably about 200 nm. The current density versus voltage characterization **505** under a 1SU calibrated solar simulator show diode-like behavior with open-circuit voltage of 0.628 V and current density of 3.16 mA/cm^2. The fill factor and the overall efficiency have been calculated as 32.41% and 0.71%. OPVs fabricated with NCMIn anode show similar results as conventional ITO/PEDOT:PSS based OPVs manufactured in air,

In an embodiment, the cathode and anode of a polymer solar cell comprises an NCM according to the present disclosure. In FIG. **5**, both the TCO/HCL and HBL/metal have been replaced by the present NCMs **504**. NCMIn **524** may be used as an anode collector element and NCMAl **564** may be used as a unique cathode collector element to achieve semi-transparent OPVs. In an embodiment, NCMIn **524** and NCMAl **564** were spray coated respectively on the substrate and the photoactive layer in air. The current density versus voltage characterization **506** under a 1SU calibrated solar simulator show ohmic behavior with open-circuit voltage of 0.288 V and current density of 0.153 mA/cm^2. The fill factor and the overall efficiency have been calculated as 26.76 % and 0.0118%. OPVs fabricated using NCMIn anode and NCMAl cathode show potential as energy harvesting device considering the flexibility and the semi-transparency nature of the devices This configuration should give a VOC of approximately 250mV if one refer to the relative workfunction values measured FIG. **3**. The experimental value of 288mV obtained indicates that the NCM can be controlled and the results predictable to some extent; the poor fill factor and short-circuit current density can be considered as sign of a low quality bulk hetero-junction.

A conventional OLED may have a similar structure than a conventional OPV **501**, and may be composed of a transparent or semi-transparent carrier substrate **510** typically glass or polyethylene terephthalate (PET), an anode electrode **520** typically ITO **522**, a hole collector layer (HCL) **530** typically PEDOT:PSS, a emissive polymer **540** typically poly(9,9-di-n-dodecylfluorenyl-2,7-diyl) (PFOD), an optional hole blocking layer **550**, and an cathode electrode **560** typically aluminum **562**. The emissive polymer may be made by dissolving 20 mg/ml of PFOD in toluene and stirring for approximately 12 hours at 45 ^{o}C in air. The obtained PFOD emissive polymer solution is subsequently filtered with a 0.45 μm polypropylene ("PP") syringe filter in order to remove any undissolved cluster. The Al cathode is usually deposited using physical vapor deposition at base pressure of 1 μTorr and deposition rate of 1.5 Ang/s. In an embodiment, the anode of an OLED comprises an NCM according to the present disclosure. In **FIG. 7**, the TCO/HIL have been replaced by an NCM **701.** NCMIn may be used as an anode collector element and aluminium may be used as a cathode collector element. NCMIn **720** may be spray coated on top of the carrier substrate **710**, followed subsequently by spray coating of the PFOD layer **730** and physical vapor deposition of the Al layer **740**. The flat band energy diagram **702** shows the expected energy level alignment of an OLED made using NCMIn. An NCMIn OLED of approximately 3 mm by 3 mm pixel was subjected to a bias voltage of 15 V and exhibits electroluminescence **704** within the usual range of potential and current.

FIG. 8 shows a scanning electron microscopy (SEM) **800** of nano-hole arrays of 500 nm in periodicity and hole diameters of 100 nm created using a focused ion beam on 500 nm of one instance of the NCMAg spray coated on a glass substrate in air. It should be noted that the milling was done using a gallium ion (Ga+) source of a FEI Strata Dualbeam 235 at 1000 pA, and no additional conductive coating was deposited onto the surface of the NCMAg to increase it conductivity. The SEM images display what seem to be perfect circular hole which assess the stability of the invention to withstand high energy ionic beams and the conductive nature of the NCM since no charging effects were observed. Plot **810** of FIG. 8 shows transmission curves **812**, **814** of intensity versus wavelength of NCMAg without and with a 500 nm periodicity nanohole array. According to these results, the addition of nanohole array onto the NCMAg film can be attributed to an increase of absorption in the visible range due to surface plasmonic resonance that is commonly observed in nanostructured conductive surface. The absorption, thus the surface plasmonic response of the NCM can be tuned by using nanostructured materials.

It should be noted that, in addition to nanoparticle size, the material can be chosen according to thermodynamic stability in strongly acidic environment like titanium oxides (TixOy), cobalt oxides (CoxOy) or niobium oxides (NbxOy) for instance. This can also be used to generate and tune these plasmon resonances in the NCM. NCM with nanostructures can also be used as a diffraction grating. For instance under normal light incidence, the NCMAg with nanohole arrays of 500 nm in periodicity will diffract the first order wavelengths below 500 nm. **FIG. 9** shows an embodiment in which it may be used to replace the flexible or semi-flexible substrates as well as the buffer layer or hole injection/collector layer(s) and the electrode(s) with a NCM. A flexible OPV **900** is composed of a flexible and transparent or semi-transparent carrier substrate **960** typically PET, an anode electrode **950** typically ITO, a hole collector layer (HCL) **942** typically PEDOT:PSS, a photoactive polymer **932** typically P3HT:PCBM, an optional hole blocking layer **920** typically calcium, and an cathode electrode **910** typically aluminum. Upon illumination by an external light source **970**, an OPV generate current between the positive and the negative contact electrodes points. In a flexible NCM **904** the substrate/anode/HCL (PET/ITO/PEDOT:PSS) are replaced by one instance of NCM such as for instance NCMIn **990**. Additionally the buffer layer/cathode may also be replaced by one instance of NCM such as for instance NCMAl **980**. A substrate-free OPV employing NCM can achieve extreme flexibility, transparency and lightweight. Combined with deposition technique such as spray coating, ink jet printing and brush painting, NCM substrate-free OPVs are suitable for wearable electronics, and none uniform surfaces and geometries.

In an embodiment, a flexible OLED **902** is composed of a flexible and transparent or semi-transparent carrier substrate **960** typically PET, an anode electrode **950** typically ITO, a hole inject layer (HIL) **944** typically PEDOT:PSS, an emissive polymer **934** typically PDOF, an optional hole blocking layer **920**, and an cathode electrode **910** typically aluminum. Upon applying a bias, electroluminescence can be observed **971**. In a flexible NCM, the substrate/anode/HIL (PET/ITO/PEDOT:PSS) are replaced by one instance of NCM **906** such as for instance NCMIn **990**. Additionally the buffer layer/cathode may also be replaced by one instance of NCM such as for instance NCMAl **980**. A substrate-free OLED employing NCM can achieve extreme flexibility, transparency and lightweight. Combined with deposition technique such as, but not limited to, spray coating, ink jet printing and brush painting, NCM substrate-free OLEDs are suitable for wearable electronics, and none uniform surfaces and geometries.

In an embodiment, a flexible organic diode or flexible organic transistor may also be constructed by replacing the anode/buffer layers and cathode/buffer layers by one instance of NCM. Combined with deposition technique such, but not limited to, as spray coating, ink jet printing and brush painting, NCM substrate-free OLEDs are suitable for wearable electronics, and none uniform surfaces and geometries.

FIG. 10 shows an embodiment in which it may be used as flexible or semi-flexible and transparent or semi-transparent conductive sheets or substrate. In one embodiment NCM **1000** made using for instance spray coating **1002** or doctor blading **1004** can be used to deposit a metal layer using electrochemical deposition (ECD). The ECD of metals and semiconductors on substrates is an important manufacturing process for esthetic purposes and to electrode patterning in electronics, optics, electromagnetic shielding and interconnect manufacturing. ECD provides the ability to cover large scale surfaces with patterns and structures down to the nm scale with more precise control over the grain size and texture of the deposited materials. This reduces the occurrence of voids and gaps inherent to physical vapor deposition techniques. Additionally, the unmatched of filling and super conformal deposition even for arbitrary 3D geometries mean ECD is the prevalent technique in the production of complex interconnects and conductive coating. Embodiments of the present NCMs are resistant to solvation by water and exhibit good conductivity, which allows the NCMs to meet the requirements as a substrate material for ECD. Deposition methods such as screen printing, casting, blading, spray coating, spin coating, paint brushed, die slot, jet printed, inkjet printing, 3D printing, molding, stamping, etching, or a combination thereof, the NCMs can be pattern in various shapes and forms, and thereafter subjected to ECD. Various materials can be deposited down to the nanometer scale, producing multi layered structured with tunable functionalities. In one embodiment in which it may be advantageous to have both conductivity and transparency or semi-transparency, a thin sheet, substrate or layer of NCM **1000** made using for instance, but not limited to, spray coating **1002** or doctor blading **1004** can be used as an electromagnetic shield on windows, electronics, and automotive, or as TCO replacement in electrochromic devices, wearable electronic, and defrosting coating, for example.

In one embodiment a flexible LED panel “OFF” **1010** and “ON” **1012** using NCM as interconnects material can be patterned using for instance spray coating, jet printing, ink jet printing, screen printing or a combination thereof. It may be beneficial to use flexible LED panels in products such as advertisement, flying banners, wearable electronics, automotive and consumer electronics. In one embodiment it may be advantageous to use the NCM as ink formulation for 3D printing and ink jet printing allowing complex and advanced electronic devices to be made. The NCM ink viscosity may be adjusted using additional solvent such as 1-propanol, dimethylsulfoxide, or 2-propanol, or combination thereof, for instance.

FIG. **1** illustrates the physical structure at the origin of the chemico-physical properties of the NCM.

FIG. **2** presents an SEM profiles of one instance of the NCM.

FIG. **3** presents transport, valence band and workfunction measurements of several examples of the NCM on glass substrate with approximately 300nm in thickness.

FIG. **4** shows the characterization of the mechanical properties, solvent resistance and heat resistance of one example of the NCM with approximately 300nm in thickness sprayed on cellulose acetate film compared to a purchase PET substrate with 100nm of ITO.

FIG. **5** presents designs and data characterizing the usage of two examples of the NCM in OPVs fully spray coated in air.

FIG. **6** presents designs and data characterizing the usage of the NCM in semi-conductor/metal hetero-junctions.

FIG. **7** shows designs and data characterizing the usage of an instance of the NCM in OLEDs spray and spin coated in air.

FIG. **8** shows SEM and transmission spectrum with and without the nano-hole array created using FIB on 500 nm of one instance of the NCM spray on a glass slide.

FIG. **9** shows a comparison of typical electro-optical films and those comprising the present NCMs.

FIG. **10** shows spray coated and doctor bladed NCM films, and a LED panel using NCM interconnects

It is contemplated that any embodiment discussed in this specification can be implemented or combined with respect to any other embodiment, method, composition or aspect of the invention, and vice versa.

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[C. Zaluski et al., 1994] "Blends of Nafion and Dow Perfluorosulfonated Ionomer Membranes", Macromolecules 1994, 27, 6150-6754.

All citations are herein incorporated by reference, as if each individual publication was specifically and individually indicated to be incorporated by reference herein and as though it were fully set forth herein. Citation of references herein is not to be construed nor considered as an admission that such references are prior art to the present invention.

The invention includes all embodiments, modifications and variations substantially as hereinbefore described and with reference to the examples and figures. It will be apparent to persons skilled in the art that a number of variations and modifications can be made without departing from the scope of the invention as defined in the claims. Examples of such modifications include the substitution of known equivalents for any aspect of the invention in order to achieve the same result in substantially the same way.

The present invention may be illustrated by reference to examples, embodiments or the like. However it is to be understood that these are for illustrative purposes only, and should not be used to limit the scope of the present invention in any manner.

CLAIMS

1. A nanocomposite conducting matrix comprising:
   a) at least one electron donor substance,
   b) at least electron acceptor substance, and
   c) at least one nanoparticle.

2. The nanocomposite conducting matrix according to claim 1 wherein the at least one electron donor substance is selected from poly(fluorine)s, polyphenylenes, polypyrenes, polyazulenes, polynaphthalenes, poly(acetylenes)s (PAC), poly(p-phenylene vinylene) (PPV), poly(pyrrole)s (PPY), polycarbazoles, polyindoles, polyazepines, polyanilines (PANI), poly(thiophene)s (PT), or combinations thereof.

3. The nanocomposite conducting matrix according to claim 1 wherein the at least one electron acceptor substance is selected from hydrogenated polymers, partially fluorinated polymers or perfluorinated polymers and/or copolymer comprising at least one carbonate and/or one sulfonate end-group like sulfonated polycarbonates, polystyrene sulfonates, polyvinyl sulfonates, perfluorosulfonic acid polymers or perfluorosulfonic acid based copolymers, polystyrene carboxylates, polyvinyl carboxylates, perfluorocarboxylic acid polymers, perfluorocarboxylic acid based copolymers, or combinations thereof.

4. The nanocomposite conducting matrix according to claim 1 wherein the at least one electron acceptor substance is selected from perfluorosulfonic acid-PTFE copolymers with side chains having three or two fluoro-substituted carbon atoms.

5. The nanocomposite conducting matrix according to claim 1 wherein the composite comprises poly(styrene sulfonic acid).

6. The nanocomposite conducting matrix according to claim 1 wherein the at least one nanoparticle is selected from pure and/or oxide compounds include, but are not limited to, those comprising aluminum, zinc, magnesium, manganese, copper, indium, silicon, chromium, nickel, iron, titanium, vanadium, strontium, cobalt, niobium, ruthenium, silver, palladium, platinum, gold, graphene, yttrium, barium, calcium, or a suitable combinations thereof.

7. The nanocomposite conducting matrix according to claim 1 wherein the at least one nanoparticle comprises a metal ion selected from those having a s-type electron sub-shell.

8. The nanocomposite conducting matrix according to claim 1 wherein the at least one nanoparticle comprises a metal ion selected from those having a p-type, d-type, or f-type electron sub-shell.

9. An electro-optical device comprising the nanocomposite conducting matrix according to claim 1 and a substrate.

10. An electro-optical device comprising the nanocomposite conducting matrix according to claim 1 and a flexible substrate.

11. An electro-optical film comprising a cathode layer, a photoactive layer, and an anode layer; wherein the cathode layer, the anode layer, or both comprises the nanocomposite conducting matrix according to claim 1.

12. An electro-optical device comprising the nanocomposite conducting matrix according to claim 1, wherein the device is selected from electrochromic devices.

13. A method of patterning the conducting track of an electronic circuit on a substrate, said method comprising applying the nanocomposite conducting matrix according to claim 1 to the substrate.

14. A method of patterning the conducting track of an electronic circuit on a substrate, said method comprising applying the nanocomposite conducting matrix according to claim 1 to the substrate wherein the conductivity of said substrate is greater than about 1500S/cm.

15. Use of the nanocomposite conducting matrix according to claim 1 as an electromagnetic shielding material.

16. Use of the nanocomposite conducting matrix according to claim 1 as a seed layer for electroplating thin film metals or semi-conductors.

17. A method of adjusting the workfunction of a nanocomposite conducting matrix, said method comprising:

determining if an increased or decreased workfunction is required, and

providing a nanocomposite conducting matrix according to claim 1 wherein the nanoparticle comprises a metal ion having a lower valence when increased workfunction is required or higher valence when decreased workfunction is required..

18. A process for manufacturing the nanocomposite conducting matrix according to claim 1.

19. A process for manufacturing the nanocomposite conducting matrix according to claim 1 in the form of sheets, substrate, foam, coating, rods, wires, particles and crystals down to the nanometer size.

20. A method of manufacturing a multi layered structure, comprising screen printing, blading, spray coating, spin casting, paint brushing, slot die, jet printing, inkjet printing, 3D printing the nanocomposite conducting matrix according to claim 1 to a substrate.

21. A method of manufacturing a multi layered structure, comprising screen printing, blading, spray coating, spin casting, paint brushing, slot die, jet printing, inkjet printing, 3D printing the nanocomposite conducting matrix according to claim 1 to a flexible substrate.

22. A method of using the nanocomposite conducting matrix according to claim 1 as a conductive coating or seed layer for electrochemical deposition of at least one layer of metallic or semiconductor material.

23. A method of using the nanocomposite conducting matrix according to claim 1 as a conductive coating for electromagnetic shielding and/or defrosting coating.

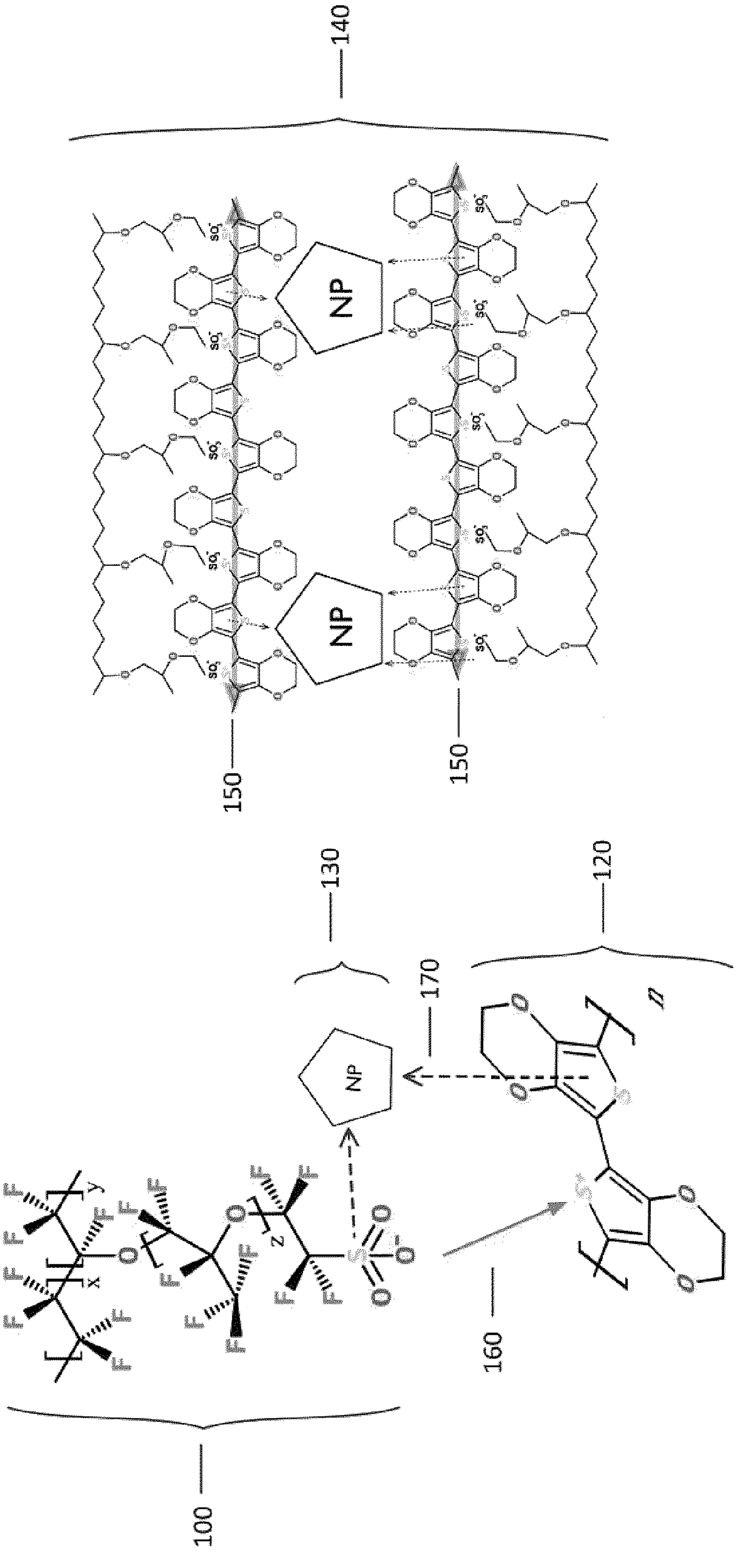
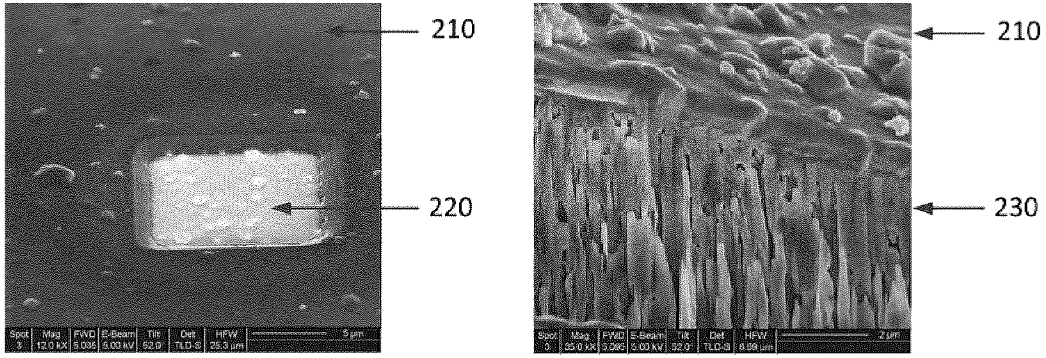


FIG.1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220
Spot
3
Mag
12.0 kX
FWD
5.035
E-Beam
5.00 kV
Tilt
52.0°
Det
TLD-S
HFW
25.3 µm
5 µm
210
230
Spot
3
Mag
35.0 kX
FWD
5.095
E-Beam
5.00 kV
Tilt
52.0°
Det
TLD-S
HFW
8.69 µm
2 µm

FIG.2

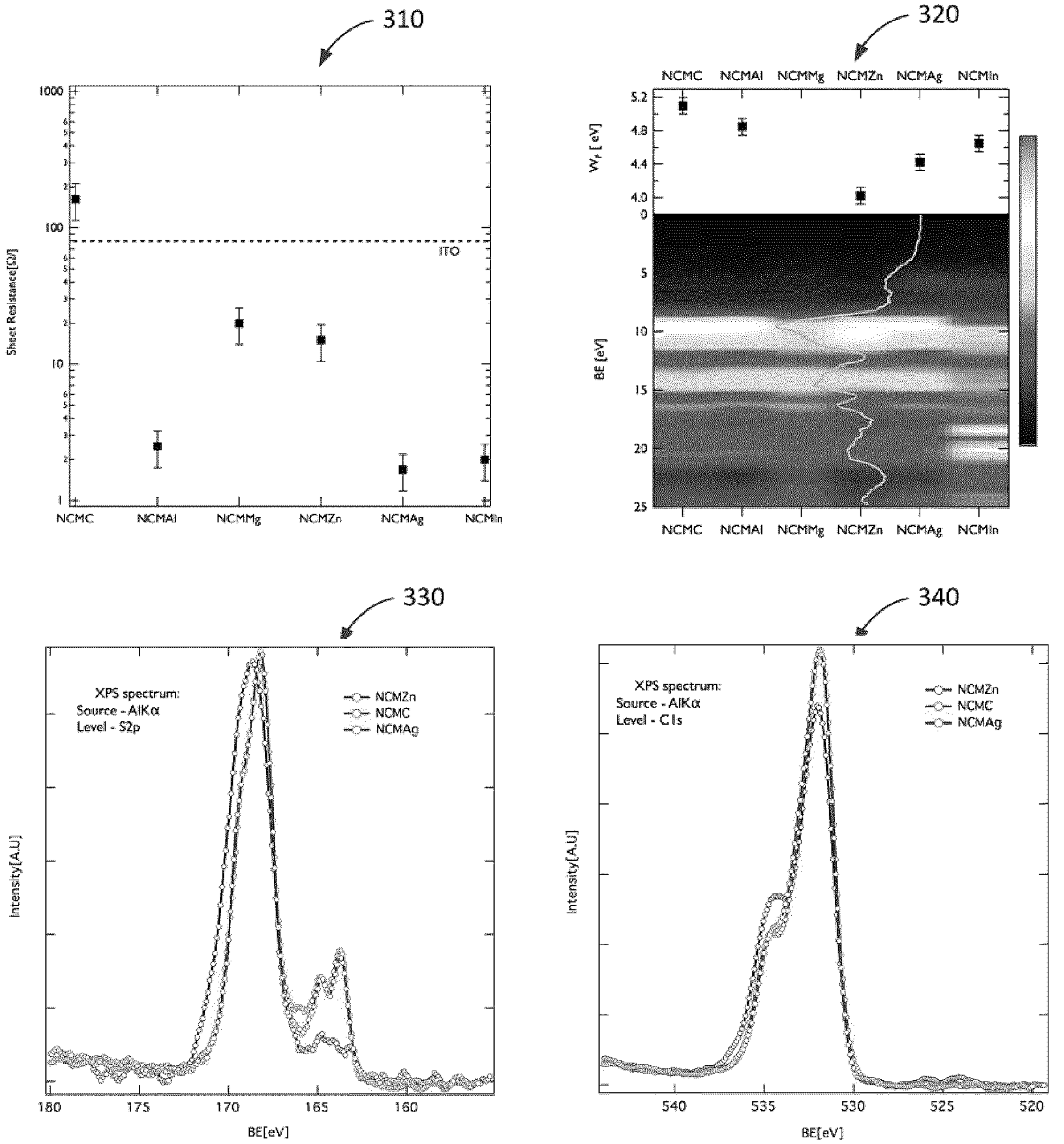
310
Sheet Resistance[Ω]
1000
100
10
1
ITO
NCMC
NCMAl
NCMMg
NCMZn
NCMAg
NCMIn
320
NCMC
NCMAl
NCMMg
NCMZn
NCMAg
NCMIn
W_f [eV]
5.2
4.8
4.4
4.0
0
5
10
15
20
25
BE [eV]
NCMC
NCMAl
NCMMg
NCMZn
NCMAg
NCMIn
330
XPS spectrum:
Source - AlKα
Level - S2p
NCMZn
NCMC
NCMAg
Intensity[A.U]
180
175
170
165
160
BE[eV]
340
XPS spectrum:
Source - AlKα
Level - C1s
NCMZn
NCMC
NCMAg
Intensity[A.U]
540
535
530
525
520
BE[eV]

FIG.3

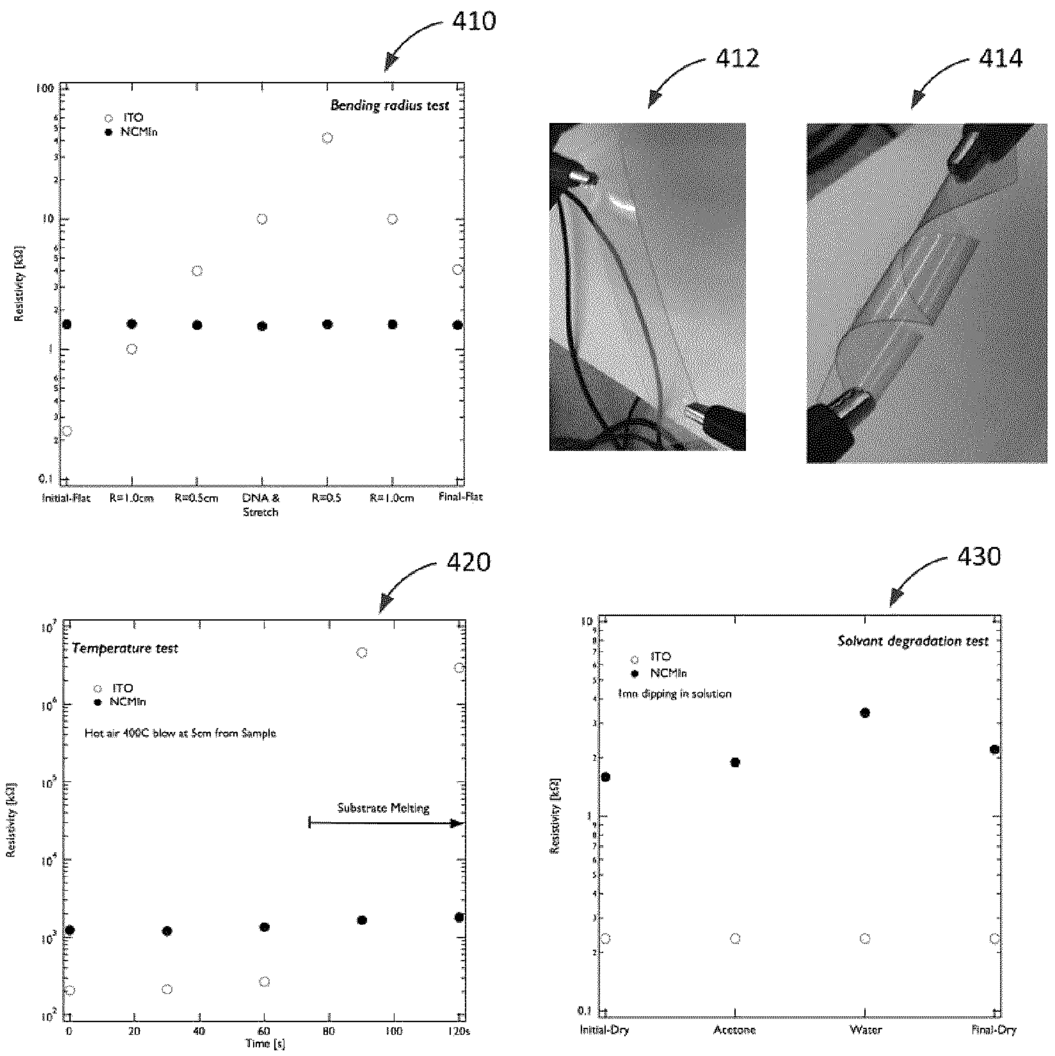
410
Bending radius test
ITO
NCMIn
Resistivity [kΩ]
100
10
1
0.1
Initial-Flat
R=1.0cm
R=0.5cm
DNA & Stretch
R=0.5
R=1.0cm
Final-Flat
412
414
420
Temperature test
ITO
NCMIn
Hot air 400C blow at 5cm from Sample
Substrate Melting
Resistivity [kΩ]
10^7
10^6
10^5
10^4
10^3
10^2
0
20
40
60
80
100
120s
Time [s]
430
Solvant degradation test
ITO
NCMIn
1mn dipping in solution
Resistivity [kΩ]
10
1
0.1
Initial-Dry
Acetone
Water
Final-Dry

FIG.4

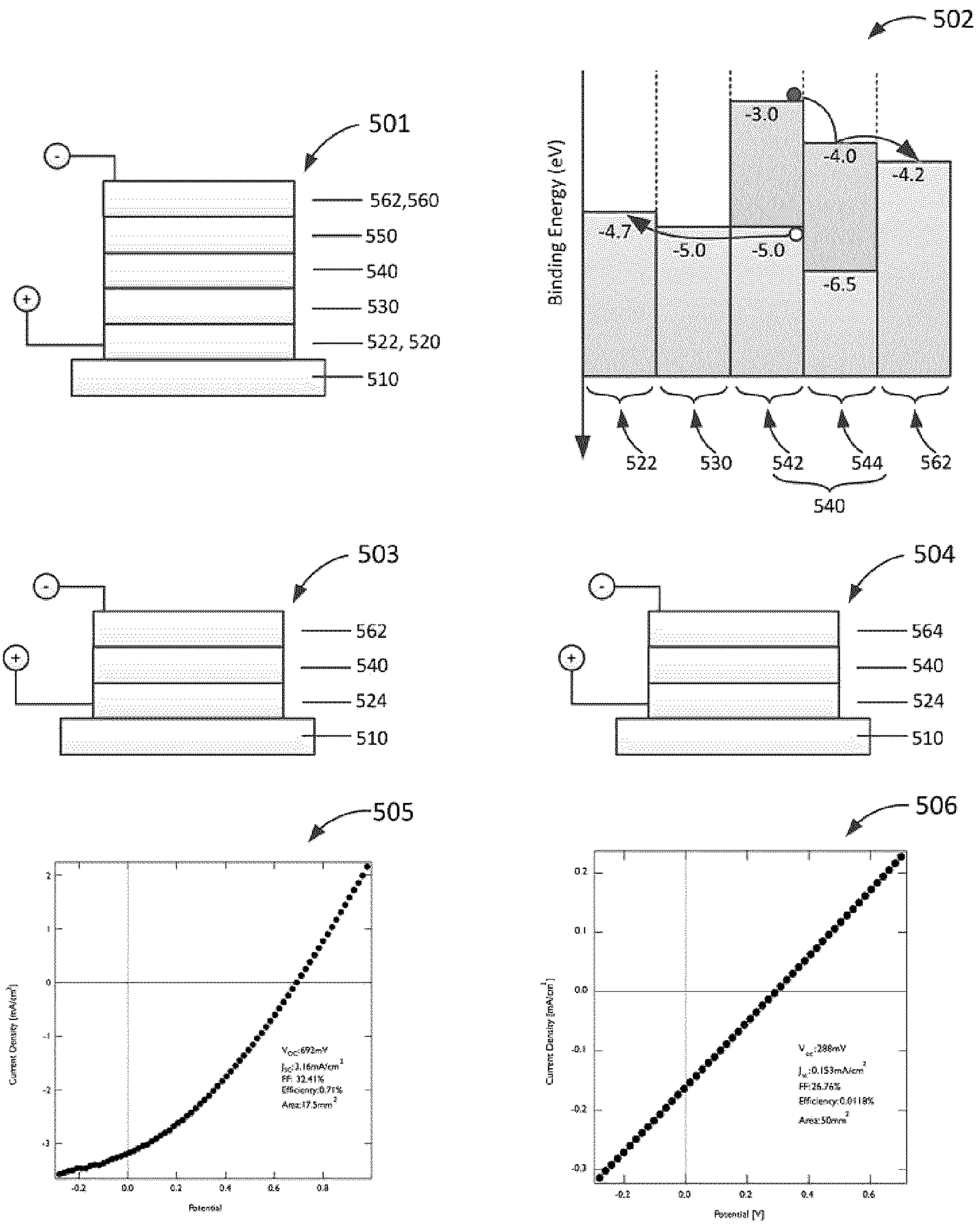
501
-
+
562,560
550
540
530
522, 520
510
502
Binding Energy (eV)
-4.7
-5.0
-3.0
-5.0
-4.0
-6.5
-4.2
522
530
542
544
562
540
503
562
540
524
510
504
564
540
524
510
505
2
1
0
-1
-2
-3
Current Density [mA/cm²]
-0.2
0.0
0.2
0.4
0.6
0.8
Potential
V_{OC}:692mV
J_{SC}:3.16mA/cm^2
FF: 32.41%
Efficiency:0.71%
Area:17.5mm^2
506
0.2
0.1
0.0
-0.1
-0.2
-0.3
Current Density [mA/cm²]
-0.2
0.0
0.2
0.4
0.6
Potential [V]
V_{oc}:288mV
J_{sc}:0.153mA/cm^2
FF:26.76%
Efficiency:0.0118%
Area:50mm^2

FIG.5

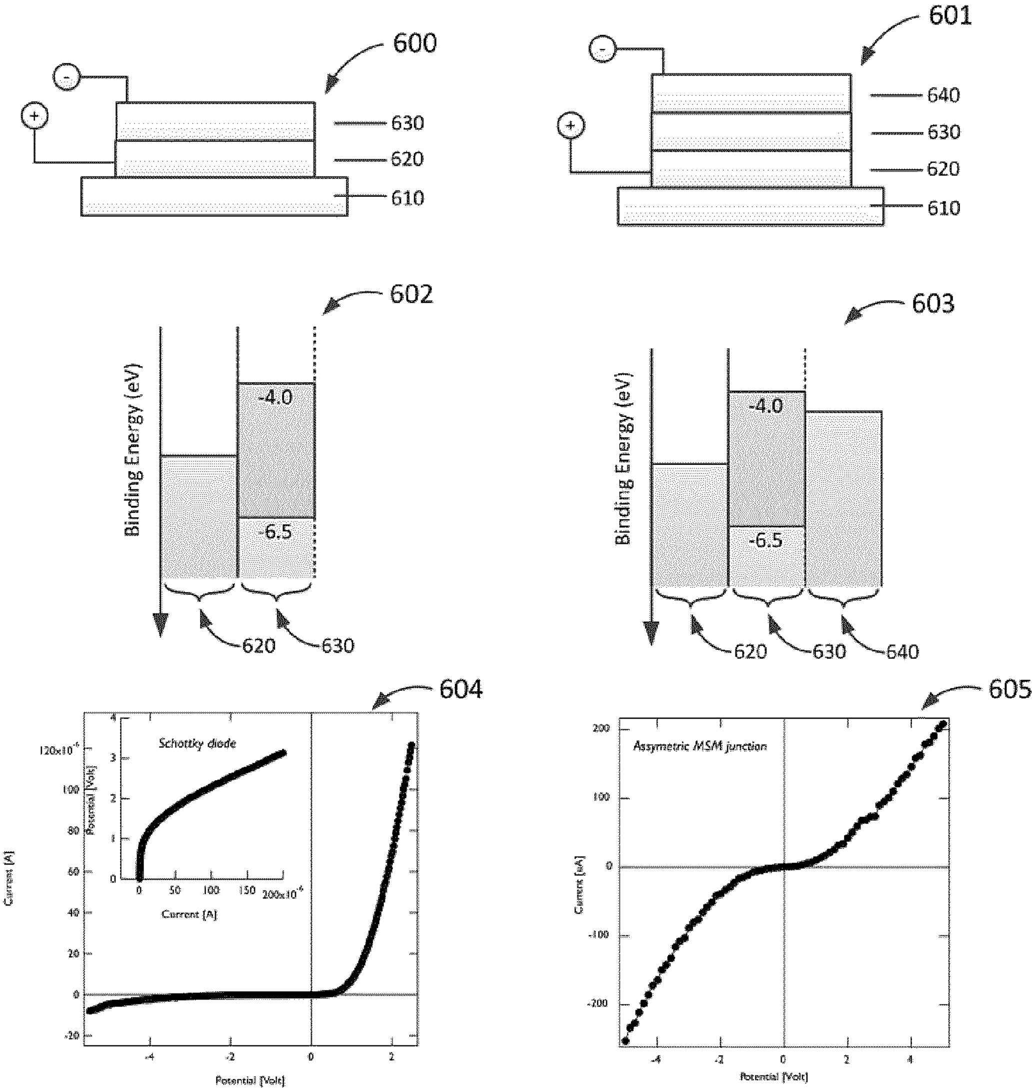
600
630
620
610
601
640
630
620
610
602
Binding Energy (eV)
-4.0
-6.5
620
630
603
Binding Energy (eV)
-4.0
-6.5
620
630
640
604
Current [A]
120x10^-6
100
80
60
40
20
0
-20
-4
-2
0
2
Potential [Volt]
Schottky diode
Potential [Volt]
4
3
2
1
0
0
50
100
150
200x10^-6
Current [A]
605
Assymetric MSM junction
Current [uA]
200
100
0
-100
-200
-4
-2
0
2
4
Potential [Volt]

FIG.6

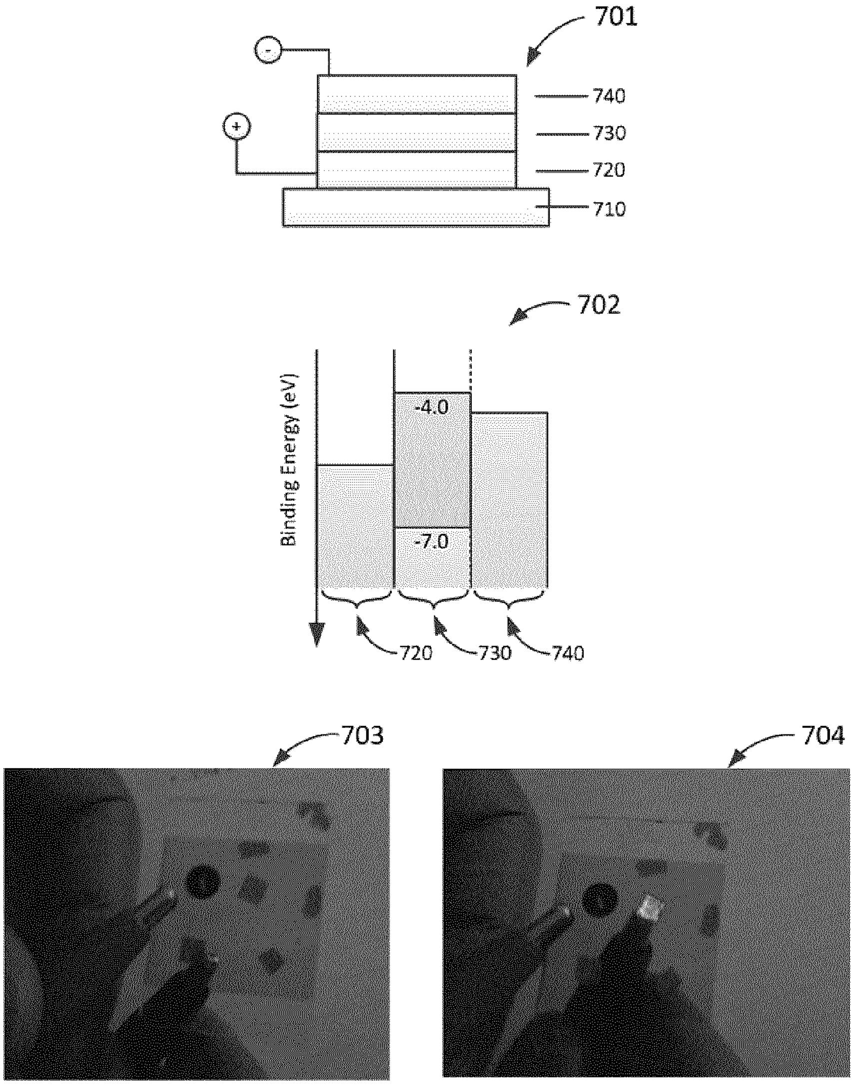
701
-
+
740
730
720
710
702
Binding Energy (eV)
-4.0
-7.0
720
730
740
703
704

FIG.7

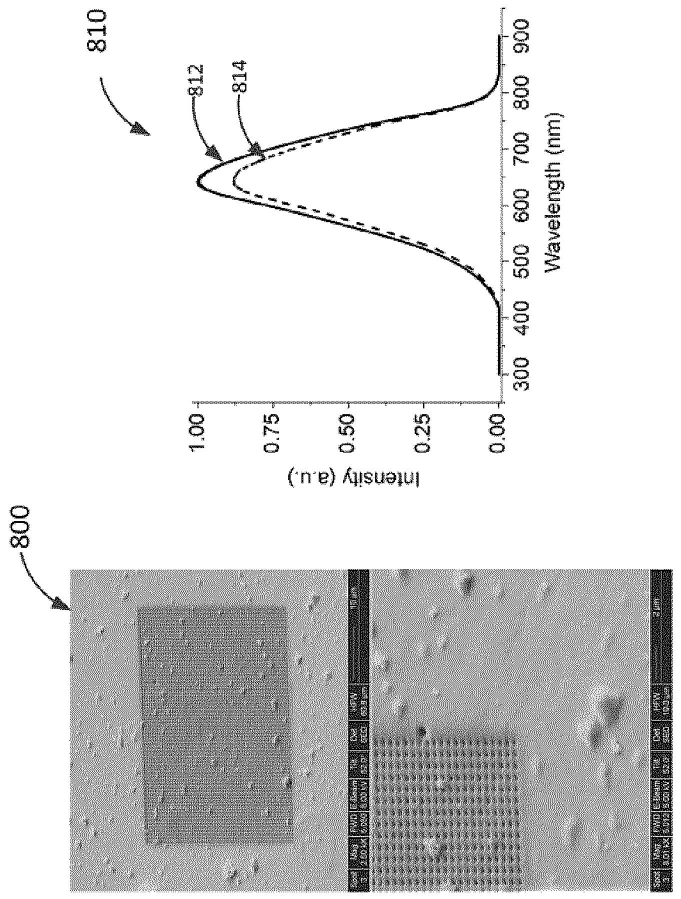
810
812
814
Intensity (a.u.)
1.00
0.75
0.50
0.25
0.00
300
400
500
600
700
800
900
Wavelength (nm)
800
10 µm
2 µm

FIG.8

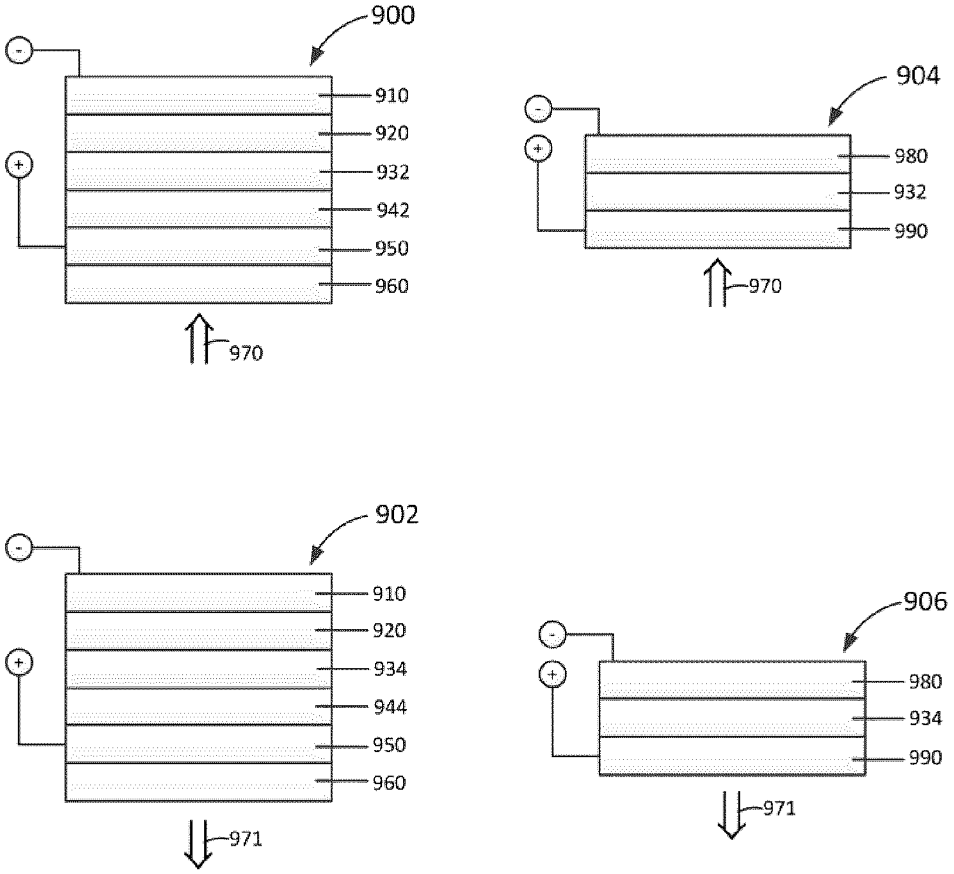
900
-
+
910
920
932
942
950
960
970
904
-
+
980
932
990
970
902
-
+
910
920
934
944
950
960
971
906
-
+
980
934
990
971

FIG.9

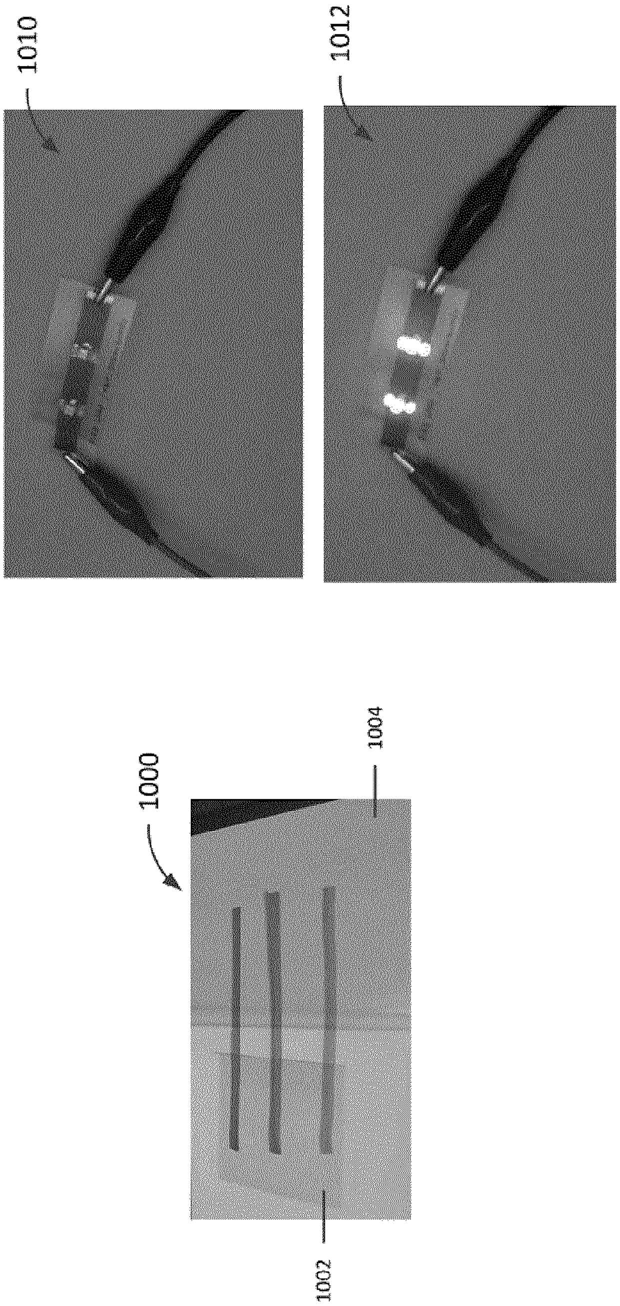

FIG.10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2013/050968

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***H01B 1/00*** (2006.01) , ***B32B 37/00*** (2006.01) , ***B82Y 30/00*** (2011.01) , ***C08K 3/00*** (2006.01) , ***C08L 101/12*** (2006.01) , ***C09D 5/24*** (2006.01)
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: ***H01B 1/00*** (2006.01) , ***B32B 37/00*** (2006.01) , ***B82Y 30/00*** (2011.01) , ***C08K 3/00*** (2006.01) , ***C08L 101/12*** (2006.01) , ***C09D 5/24*** (2006.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Databases: Google Patent, TotalPatent, Canadian Patent database.
Keywords: nanocomposite, electron donor, acceptor, nanoparticle, matrix.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/024461 A2 01 March 2007 (01-03-2007) Rao et al. (see page 23, line 25-page 24, line 3; page 22, lines 30-31; page, 14, lines 7-21; page 15, line 26-page 16, line 26; page 24, lines 30-31; page 27, line 1; page 7, line 20-page 8, line 11)	1-3, 6, 7, 8-10, 15, 18, 23
X	WO 2007/072139 A2 28 June 2007 (28-06-2007) Nguyen etal. (see page 4, lines 5-24; page 10, lines 2-21; page 10, line 39; page 11, line 3; page 9, lines 3-13; abstract; page 5, lines 23-25)	1-3, 5, 6, 8-10, 18, 22
X	US 2010/0247870 A1 30 September 2010 (30-09-2010) Suzuki et al. (see [0107]-[0112]; [0091]; [0092]; [156]; [0182]-[0184]; [0033]-[0047]; [0100]-[0107]; [0144]	1-3, 4, 6, 7, 8-10, 13, 14, 18, 19, 21
X	WO 2010/051102 A1 06 may 2010 (06-05-2010) Rouse (see [0056]; [0060]; [0074]; [0072]; figure 1, abstract; [0188]-[0194]; [0084]; [0072]-[0075];	1-3, 6, 7, 8-10, 11, 12, 16, 17, 18, 20,21

[ ] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"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
February 18, 2014 (12-02-2014)

Date of mailing of the international search report
18 February 2014 (18-02-2014)

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Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 001-819-953-2476

Authorized officer

Thomas KC. Tang (819) 997-2189

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2013/050968

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
WO2007024461A2	01 March 2007 (01-03-2007)	US2007042174A1 US7569254B2 WO2007024461A3	22 February 2007 (22-02-2007) 04 August 2009 (04-08-2009) 18 May 2007 (18-05-2007)
WO2007072139A2	28 June 2007 (28-06-2007)	EP1949484A2 US2007077478A1 WO2007072139A3	30 July 2008 (30-07-2008) 05 April 2007 (05-04-2007) 15 November 2007 (15-11-2007)
US2010247870A1	30 September 2010 (30-09-2010)	JP5353705B2 US8456005B2 WO2009054273A1	27 November 2013 (27-11-2013) 04 June 2013 (04-06-2013) 30 April 2009 (30-04-2009)
WO2010051102A2	06 May 2010 (06-05-2010)	EP2331628A2 JP2012502144A KR20110059759A US2011204281A1 US8414792B2 WO2010051102A3	15 June 2011 (15-06-2011) 26 January 2012 (26-01-2012) 03 June 2011 (03-06-2011) 25 August 2011 (25-08-2011) 09 April 2013 (09-04-2013) 24 June 2010 (24-06-2010)