

METHOD FOR FORMING A TRANSPARENT CONDUCTING POLYMERIC FILM AND ITS USE AS A TRANSPARENT ELECTRODE

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of priority of United States of America Provisional Patent Application No. 61/983,607, filed April 24, 2014, the contents of which being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

The invention relates generally to a method for forming transparent electrodes. In particular, the transparent electrodes are comprised of a transparent conducting polymeric film. Conductive elements are embedded in the transparent conducting polymeric film during the formation process. The transparent conducting polymeric films are useful in electrochromic devices or piezochromic devices.

BACKGROUND

With the growing sophistication of consumer electronics, especially after the unveiling of the world's first full-coloured bendable display by Samsung Electronics at the Consumer Electronics Show (CES) 2013, there is growing need for transparent but yet conducting substrate to realize the next generation of consumer devices. The demand is also fuelled on the other spectrum with calls for greener buildings in which the use of smart windows, touted to be electrochromic based that needs a transparent and yet conducting substrate. They both share one key component in their architecture: transparent electrode (TE). Devices such as electrochromic smart windows would not have been possible without suitable TEs. As such, the development of TEs is an important stepping-stone to realize an economical and all-solution processible device.

The use of TEs has traditionally been met with indium-tin-oxide (ITO) coatings. While it has served the industry's needs for years in nearly every touch-screen and photoelectric device, efforts have now been focused to develop an alternative TE to ITO. The reasons are quite straightforward: firstly, indium, being a rare earth element, is scarce and the price for indium has been increasing steadily due to limited supply released in the market. Secondly, the resistance of ITO increases several folds when subjected to bending. This limits the use of ITO in devices where conductivity is required in flexible state, bent state or in bends and corners.

The scientific community has been active on this front, where the use of conductive polymers, carbon nanotubes, silver nanowires, graphene, and alternative oxides such as zinc oxide or fluoro-tin-oxide (FTO) has been reported. However, among all these, the use of metallic mesh or patterns appears to be promising and is one of the leading candidates to replace ITO. The cost of metal grid fabrication is low. The use of metallic mesh is attractive because the thickness of the metal line is usually > 10 nm, thus the conductivity is unaffected by electronic scattering at the grain boundary or surface roughness, which will dramatically increase the sheet resistance. In fact, the conductivity will be close to that of the bulk metal counterpart. Moreover, at high enough mesh density per inch and line widths $< 5\mu\text{m}$, the human eye will not be able to distinguish each line and will view it as a transparent continuous film. This fact has been cleverly used by Apple Inc. in its Retina™ displays. Theoretically, nanopatterned silver films can achieve a sheet resistance as low as $0.8 \Omega/\square$ and a transparency of 90 %.

SUMMARY

It is an object of the present disclosure to meet the above needs for an alternative transparent electrode to indium-tin-oxide for use in electronic devices such as electrochromic devices or piezochromic devices.

According to one aspect of the invention, there is disclosed a method for forming a transparent conducting polymeric film, wherein the transparent conducting polymeric film comprises conductive elements embedded therein. The method includes:

- depositing a first layer of conductive elements onto a first substrate;
- depositing a first layer of polymeric material onto the first layer of conductive elements; and
- curing the first layer of polymeric material to form the transparent conducting polymeric film.

In preferred embodiments, the method further includes prior to said curing, depositing a second layer of conductive elements onto the first layer of polymeric material such that the first layer of polymeric material is sandwiched between the first and second layers of conductive elements.

In preferred embodiments, the method further includes prior to said depositing of the first layer of polymeric material, depositing a first layer of electrochromic material or ion storage material onto the first layer of conductive elements such that the first layer of electrochromic material or ion storage material is sandwiched between the first layer of conductive elements and the first layer of polymeric material.

According to another aspect of the invention, there is disclosed a method for forming a transparent conducting polymeric film, wherein the transparent conducting polymeric film comprises conductive elements embedded therein. The method includes:

- depositing a first layer of conductive elements onto a first substrate;
- depositing a first layer of polymeric material onto the first layer of conductive elements;
- depositing a second layer of conductive elements onto a second substrate;
- depositing a second layer of polymeric material onto the second layer of conductive elements;
- positioning the first and second substrates such that the conductive elements of the first and second layers are aligned, wherein the first layer of polymeric material contacts the second layer of polymeric material; and
- curing the first and second layers of polymeric material to form a two-electrode transparent conducting polymeric film.

In preferred embodiments, the method further includes prior to said depositing of the first layer of polymeric material, depositing a first layer of electrochromic material or ion storage material onto the first layer of conductive elements such that the first layer of electrochromic material or ion storage material is sandwiched between the first layer of conductive elements and the first layer of polymeric material.

In preferred embodiments, the method further includes prior to said depositing of the second layer of polymeric material, depositing a second layer of electrochromic material or ion storage material onto the second layer of conductive elements such that the second layer of

electrochromic material or ion storage material is sandwiched between the second layer of conductive elements and the second layer of polymeric material.

Advantageously, present methods allows for an all-solution processible synthesis steps. Present methods further allows for a free-standing transparent conducting polymeric film to be obtained, for example, by peeling off the substrate from the cured transparent conducting polymeric film.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

Fig. 1A shows a schematic illustration of the drop-casting conductive ink onto a stainless steel mask composed of regular array of square grids laying on top of a PET substrate, according to Example 1.

Fig. 1B shows a schematic illustration of the formed conducting grids composed of silver nanoparticles which self-assembled and coalesce upon removal of the non-conducting ligands through the exposure to concentrated acid fume, according to Example 1.

Fig. 1C shows a schematic illustration of the deposited electrochemical material onto the conducting silver grid, according to Example 1.

Fig. 1D shows a schematic illustration of the deposited polymeric material onto the electrochemical active material, according to Example 1.

Fig. 1E shows an illustration of the cross-sectional schematic of the device structure just before lifting-off the substrate, according to Example 1.

Fig. 1F shows an illustration of the cross-sectional schematic of the device structure after lifting-off the substrate, according to Example 1.

Fig. 2A shows a schematic illustration of the roll-coated polymer matrix on top of the electrochromic active material and the conducting silver grid, according to Example 2.

Fig. 2B shows a schematic illustration of the cross sectional of the device structure after roll-coated with PVDF, according to Example 2.

Fig. 2C shows a schematic illustration of the cross sectional of the film structure just before lifting-off the substrate, according to Example 2.

Fig. 2D shows a schematic illustration of the cross sectional of the film structure after the film was peeled off from the substrate. The conducting Ag grid with the electrochromic active material will form the working electrode, while the conducting Ag grid with the complementary electrochromic/ion-storage material will form the counter electrode, according to Example 2.

Fig. 2E shows a schematic illustration of the cross sectional of the film structure after controlled coating the polymeric matrix of less than the silver grid height. The polymeric matrix will hold the film together with parts of the silver grid embedded in the polymer matrix, according to Example 2.

Fig. 2F shows a schematic illustration of transparent conducting film where both sides are conductive, according to Example 2.

Fig. 2G shows UV-Vis spectra showing the change in transmission of the film at various voltage bias. At -1.2 V, a contrast (ΔT) of 20% is obtained, according to Example 2.

Fig. 3A shows conducting silver grids on PET substrate, according to Example 3.

Fig. 3B shows transparent conducting electrode composed of Ag grids embedded in polymer matrix, according to Example 3.

Fig. 3C shows transparent conducting electrode composed of Ag grids embedded in polymer matrix and remains conductive, according to Example 3.

Fig. 3D shows UV-VIS spectra of transparent conducting electrode composed of Ag grids embedded in polymer matrix in LiClO_4 /polycarbonate electrolyte, according to Example 3.

Fig. 3E shows optical microscope micrograph (50x) of transparent conducting electrode composed of the released Ag grids embedded in polymer matrix, according to Example 3.

Fig. 3F shows a schematic of the fabricated two-electrode solid-state electrochromic device prototype, according to Example 3.

Fig. 3G and Fig. 3H show, respectively, the coloured state and the subsequent bleaching state of the PVDF two-electrode electrochromic device, according to Example 3.

Fig. 4A shows a schematic illustration of the roll-coated polymer matrix on top of the conducting silver grid, according to Example 4.

Fig. 4B shows a schematic illustration of the cross-section of the device structure after roll-coating with PVDF, according to Example 4.

Fig. 4C shows a schematic illustration of the cross-section of the device structure after roll-coating with PVDF and spray coated with Ag NW network, according to Example 4.

Fig. 4D shows a schematic illustration of the cross-section of the double-sided free-standing conductive films composed of Ag grid on one side and Ag NW network on the other, according to Example 4.

Fig. 4E shows a schematic illustration of the cross-section of the substrate after the spray coating process of Ag NW network, according to Example 4.

Fig. 4F shows a schematic illustration of the cross-section of the device after Ag NW deposition and roll-coated with PVDF polymeric matrix, according to Example 4.

Fig. 4G shows a schematic illustration of the cross-section of the device after Ag NW deposition following roll-coating of PVDF polymer matrix, according to Example 4.

Fig. 4H shows a schematic illustration of the cross-section of the double-sided free-standing conductive films composed of Ag NW network on both sides, according to Example 4.

Fig. 5A shows a schematic illustration of the cross-section of PVDF film with metallic Ag-grid and PEDOT:PSS embedded in the polymeric matrix, according to Example 5.

Fig. 5B shows UV-Visible spectra of PVDF film with embedded PEDOT:PSS and Ag grid showing the initial (0 V bias) and coloured (-0.9 V bias) state of the film, according to Example 5.

Fig. 5C shows dynamic optical transmittance measurement of a single colour and bleach cycle showing a fast switching speed between coloured (2s) and bleached (10s) states, according to Example 5.

Fig. 5D shows dynamic optical transmittance measurement of PVDF film with embedded PEDOT:PSS and Ag grid showing a consistent cyclic stability of about 500 cycles at -0.9 and 0.2V, according to Example 5.

Fig. 6 shows UV-Visible spectra showing the transmittance of Ag-grid on PET substrate with 100 μm opening (red) and 80 μm opening (black), according to Example 6.

DESCRIPTION

The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

Electrochromism may be described as a persistent, reversible colour and/or opacity change of a material upon application of a voltage across the material. Generally, electrochromic materials demonstrate a memory effect, in that reversal of colour and/or opacity does not take place until an oppositely polarized potential is applied. In other words, a burst of electricity is required to change colour and/or opacity of the electrochromic materials, but once the change has been effected, electricity is not required to maintain the change. Typically, energy required to drive electrochromic materials is very low, involving an operating potential of only a few volts. This makes electrochromic devices very attractive due to their low energy consumption. In a typical electrochromic device, an electrochromic material (usually a transition metal oxide but not necessarily so) is sandwiched in between two conducting electrodes (working and counter electrode) that is separated by an ionically conducting electrolyte (sol-gel based in an all-solid device).

According to various embodiments, there is disclosed a method for forming a transparent conducting polymeric film, wherein the transparent conducting polymeric film comprises conductive elements and electrochromic material embedded therein. The method includes:

applying a wetting agent/surfactant onto a substrate;

depositing a layer of conductive elements onto a substrate;

depositing a layer of electrochromic material or ion storage material onto the layer of conductive elements;

depositing a layer of polymeric material onto the layer of electrochromic material or ion storage material;

curing the layer of polymeric material to form the transparent conducting polymeric film with embedded electrochromic material; and

peeling the transparent conducting polymeric film with the embedded electrochromic material from the substrate.

The thus-formed transparent conducting polymeric film with embedded electrochromic active material may be used as transparent electrodes in electrochromic devices. As used herein, the term “electrochromic device” refers to a device containing a material or compound which changes colour upon application of an electric potential. Advantageously, methods disclosed herein allow use of electrically conductive materials which may not themselves be optically transparent, to form the transparent electrode or transparent conducting polymeric film. In so doing, materials for use as transparent electrodes are not limited to indium-tin-oxide based materials, as non-indium tin oxide materials such as carbon nanotubes, graphene, and metallic nanowires or nanoparticles may be used instead. By avoiding use of indium-tin-oxide, problems associated with use of indium-tin-oxide as set out in the background section may be averted.

In various embodiments, the step of depositing any layer recited in the present methods includes deposition techniques that are low costs and preferably solution-processible, such as but not limited to, drop-casting, inkjet printing, self assembly, tailored screen printing, roll-coating, thermal evaporation, laser ablation, spray coating, dip coating, sputtering, chemical

vapor deposition (CVD), metal-organic deposition technique, spray pyrolysis, electrodeposition, and sol-gel technique, which allow large scale manufacturing to be carried out in a simple and efficient manner.

In present context, “conductive elements” refer to electrically conductive elements, components, or materials. Examples of conductive elements that may be used include, but are not limited to, a metal, an electrically conductive polymer, carbon nanotubes, graphene, reduced graphene oxide, and combinations thereof.

In various embodiments, the conductive elements are free or essentially free of indium-tin-oxide. By not using indium-tin-oxide, problems associated with indium-tin-oxide, such as brittleness and high cost of indium-tin-oxide, may be avoided.

The conductive elements may be an electrically conductive nanostructured material. As used herein, the term “nanostructured material” refers to a material having at least one dimension that is in the nanometer range. Examples of nanostructured material may include nanotubes, nanoflowers, nanowires, nanofibers, nanoflakes, nanoparticles, nanodiscs, nanosheets, and combinations thereof.

At least one dimension of the electrically conductive nanostructured material may be less than 1,000 nm. For example, the electrically conductive nanostructured material may have a size ranging from 1 nm to 1,000 nm. As the electrically conductive nanostructured material may not be regular in shape and/or be of the same shape, the term “size” as used herein refers to the maximal dimension of the electrically conductive nanostructured material in any direction.

The electrically conductive nanostructured material comprises metallic nanomaterials or alloyed nanomaterials, such as metallic nanoparticles or alloyed nanoparticles. In various embodiments, the electrically conductive nanostructured material comprises or consists of metallic nanoparticles. In specific embodiments, the electrically conductive material comprises or consists of silver. For example, the conductive elements may comprise or consist of silver nanoparticles, gold nanoparticles, copper nanoparticles, alloy nanomaterials or a mixture thereof.

The electrochromic material or ion storage material may include metal oxide films, molecular dyes, and conducting polymers. In various embodiments, the electrochromic material comprises or consists of an oxide of a metal selected from Group 3 to Group 12 of the Periodic System of Elements. For example, the metal oxide may be an oxide of a transition metal. Examples of transition metal include, but are not limited to, iridium (Ir), scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), and alloys thereof.

In various embodiments, the electrochromic material is selected from the group consisting of WO_3 , NiO , V_2O_5 , TiO_2 , MoO_3 , and combinations thereof. In some embodiments, the electrochromic material comprises or consists of a metal oxide selected from the group consisting of tungsten oxide, nickel oxide, and combinations thereof.

In specific embodiments, the electrochromic material is tungsten oxide. The tungsten oxide may have formula (WO_3). Advantageously, tungsten oxide is able to exhibit a fast response and high coloration efficiency, which renders its suitability for use as an electrochromic material.

Furthermore, it changes colour from transparent or yellow to deep blue with a large optical modulation when it is reduced under cathodic polarization, to provide a large contrast.

The electrochromic material may be an electrochromic nanostructured material. Examples of nanostructured material have already been discussed above. In various embodiments, the electrochromic nanostructured material comprises nanoparticles and/or nanorods. For example, the electrochromic nanostructured material may comprise or consist of tungsten oxide nanoparticles, tungsten oxide nanorods, nickel oxide nanoparticles, and/or nickel oxide nanorods.

In various embodiments, size of the electrochromic nanostructured material is in the range of about 10 nm to about 200 nm. For example, size of the electrochromic nanostructured material may be, but not limited to, one that is in the range of about 30 nm to about 200 nm, about 60 nm to about 200 nm, about 90 nm to about 200 nm, about 40 nm to about 150 nm, about 40 nm to about 100 nm, about 60 nm to about 150 nm, about 60 nm to about 100 nm, about 80 nm to about 100 nm, or about 70 nm, about 80 nm, about 90 nm, or about 100 nm. Advantageously, the indicated size range of electrochromic nanostructured material renders the electrochromic nanostructured material suitable for use in an ink composition for inkjet printers, as typical nozzle diameter of inkjet printers are in the range of tens of micrometers.

Size distribution of the electrochromic nanostructured material is not limited, and electrochromic nanostructured material having a wide particle size distribution or a narrow particle size distribution may be used. In some embodiments, the electrochromic nanostructured material is essentially monodisperse, whereby the term "monodisperse" refers to the nanostructured

material having at least substantially the same size. In specific embodiments, average size of the electrochromic nanostructured material is about 90 nm.

In alternative embodiments, the electrochromic material or ion storage material may be an organic-based material. For example, the electrochromic material or ion storage material may comprise or consist of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS).

The substrate may be a rigid substrate or a flexible substrate. In preferred embodiments, the substrate is a flexible substrate. In some embodiments, the substrate is selected from the group consisting of glass, polycarbonate, polyethylene terephthalate, polyethylene naphthalate, polyimide, polydimethylsiloxane, and combinations thereof. In specific embodiments, the substrate is polyethylene terephthalate.

Before depositing the conductive elements onto the substrate, the substrate may be subjected to a pre-treatment, for example, using oxygen plasma or UV-light irradiation. The pre-treatment may include immersing the substrate into a diluted wetting agent solution, such as BYK 348 and/or BYK 333 (0.5 to 5wt.%), for a suitable time duration in the range of about five seconds to about ten seconds, prior to wiping dry with a cleanroom or polyester wipe, or blow dry. Other pretreatment techniques are also suitable.

The polymeric material forms the polymeric film after curing. In present context, the polymeric material is optically transparent such that the resultant polymeric film is optically transparent. In various embodiments, the polymeric material may be selected from the group consist of polyvinyl alcohol (PVA), polyvinylidene fluoride (PVDF), polymethylmethacrylate (PMMA), polydimethylsiloxane (PDMS), poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)

(PEDOT:PSS), poly(3,4-ethylenedioxythiophene) PEDOT, polyaniline (PANI), and a mixture thereof. In preferred embodiments, the polymeric material comprises PVDF or a mixture of PVA and PMMA. The transparent conducting polymeric film is rendered conductive due to the embedded conductive elements formed therein during the deposition step.

The step of curing the polymeric material to form the polymeric film may include heating the polymeric material. In various embodiments, the polymeric material may be cured by heating on a hotplate just below its glass transition temperature to allow the polymer matrix to cure or crosslink. As the glass transition temperature of each polymeric material is different and can be readily established from known literature, a person skilled in the art would readily know at what temperature of heating to apply the curing step.

In various embodiments, the layer of conductive elements may comprise a patterned array of grid. In other words, the conductive elements may be present in a patterned arrangement, such as a grid arrangement of lines of the conductive elements, on the substrate, with at least a portion of the conductive elements in electrical contact with the electrochromic material, to form the electrochromic device.

In specific embodiments, providing a patterned arrangement of the conductive elements comprises applying a dispersion comprising the conductive elements to a template or mask arranged on the substrate, and forming the patterned arrangement of the conductive elements on the substrate by self-assembly.

For example, a patterned template may be positioned or arranged on the substrate. By depositing or drop-casting a dispersion comprising the conductive elements on the patterned

template, the dispersion comprising the conductive elements may adopt the pattern of the patterned template by self-assembly. In so doing, a patterned arrangement of the conductive elements may be obtained.

In some embodiments, providing a patterned arrangement of conductive elements may be carried out by contact printing. In such cases, the conductive elements may be applied on a template or a mold, with subsequent transfer of the conductive elements to the substrate by contacting the template or the mold with the substrate.

In specific embodiments, providing a patterned arrangement of the conductive elements is carried out by inkjet printing. Advantageously, inkjet printing as a deposition methodology allows deposition of materials of pre-defined patterns at specific locations. It also allows patterning of electrochromic materials or ion storage materials on large area flexible plastic substrates. Using inkjet printing, precise designs of patterned arrangement may be prepared using one-step processing, and involving less expensive and more compact equipment as compared to expensive photolithography methods. Conditions of printing, such as temperature of the substrate and the print-head during printing, may also be controlled easily for printing of large and uniform areas.

As used herein, the term "patterned arrangement" refers to configurations of the conductive elements, whereby the conductive elements may be placed in a regular array and/or in an irregular pattern. For example, a regular array of the conductive elements may refer to the conductive elements being arranged orderly or periodically, such as that of a grid arrangement exemplified in the examples, or in the form of electrically connected concentric circles. An irregular pattern of the conductive elements may refer to the conductive elements arranged in a

non-uniform or random fashion, with respective components of the patterned arrangement being electrically connected. The term “electrically connected” refers to the components of the patterned arrangement being arranged such that electrons are able to flow between the conductive elements in the patterned arrangement.

The patterned arrangement of the conductive elements may be any suitable arrangement that is able to effect a change in colour of an electrochromic material placed in electrical contact with the conductive elements. For example, the patterned arrangement of the conductive elements may comprise or consist of an orderly array of uniform squares, with the conductive elements forming lines that define the uniform squares. In various embodiments, the patterned arrangement comprises or consists of a grid, honeycomb, or irregular cells arrangement.

The patterned arrangement of the conductive elements may comprise lines of the conductive elements surrounding one or more of two-dimensional voids of various shapes. The term “two-dimensional voids” as used herein refer to spaces that are not occupied by the conductive elements. The conductive elements may form lines that define the various shapes. For example, the one or more of two-dimensional voids of various shapes may be a regular shape such as a square, a rectangle, a circle, a triangle, an ellipse, or a polygon, or an irregular shape.

In various embodiments, the patterned arrangement comprises or consists of a grid arrangement. The patterned arrangement may include lines of the conductive elements arranged to form a grid pattern. The lines may have a width of 50 μm or less arranged to form a grid pattern. For example, the patterned arrangement may comprise lines of the conductive elements having a width of about 0.5 μm to about 50 μm , such as about 5 μm to about 50 μm , about 15 μm to about 50 μm , about 20 μm to about 50 μm , about 30 μm to about 50 μm , about

0.5 μm to about 40 μm , about 0.5 μm to about 30 μm , about 0.5 μm to about 15 μm , about 5 μm to about 20 μm , about 20 μm to about 40 μm , or about 15 μm to about 35 μm . In specific embodiments, the patterned arrangement comprises lines having a width of about 3 μm to about 4 μm , and therefore the resulting pattern is transparent.

The patterned arrangement of the conductive elements may be sufficiently thin so as not to affect transparency. In various embodiments, thickness of the conductive elements layer may be about 50 nm to about 200 nm, such as about 50 nm to about 150 nm, about 50 nm to about 100 nm, or about 100 nm to about 200 nm.

In alternative embodiments, a thin uniform layer of conductive elements may be deposited onto the substrate. As mentioned above, any thin-film deposition techniques may be suitable. For example, the conductive elements comprising a metal nanowire network may be spray-coated onto the substrate. In another example, the conductive elements comprising a metal nanowire network may be roll-coated on the substrate.

In various embodiments, depositing the layer of electrochromic material may be carried out by a suitable thin film deposition method, such as inkjet printing, thermal evaporation, laser ablation, spray coating, dip coating, sputtering, chemical vapor deposition (CVD), metal-organic deposition technique with the use of suitable tungsten-organic compounds, spray pyrolysis, electrodeposition, and sol-gel technique.

In preferred embodiments, depositing the layer of electrochromic material may be carried out by inkjet printing. The inkjet printing may be carried out using an electrochromic ink composition comprising the electrochromic material. As mentioned above, inkjet printing as a deposition

methodology allows deposition of materials pre-defined patterns at specific locations. It involves less expensive equipment, thus rendering it a much cheaper alternative to expensive photolithography methods. Advantageously, using this methodology, a Red-Green-Blue (RGB) pixel cell electrochromic material deposition for electrochromic matrix display may be carried out. The technique may also be applied on both rigid and flexible substrates. Examples of other printing methods have already been discussed above.

In various embodiments, depositing the layer of polymeric material may be carried out by a suitable thin film deposition method, such as roll-coating, inkjet printing, thermal evaporation, laser ablation, spray coating, dip coating, sputtering, chemical vapor deposition (CVD), spray pyrolysis, electrodeposition, electropolymerization, slot die coating, Langmuir Blodgett coating and sol-gel technique etc. In preferred embodiments, the layer of polymeric material may be deposited onto the layer of electrochromic material or ion storage material by roll-coating.

Advantageously, after forming the transparent conducting polymeric film, the substrate may be removed from the layer of conductive elements, for example, by peeling off the substrate. In another example, the substrate may be selectively removed by using a delamination solution. In such a case where the polymeric material comprises PVDF, a delamination solution containing distilled water and acetone in the ratio of 1:1 may be used to remove the substrate off easily.

The method may further include immersing the transparent conducting polymeric film in an electrolyte whereby the polymeric matrix of the polymeric film acts as a medium to hold the electrolyte in place and also as a separator between the different layers.

The term “electrolyte” as used herein refers to ionic or molecular substances which, when in solution, break down or disassociate to form differently charged ions or differently charged particles.

Examples of an electrolyte include, but are not limited to, ionic liquid, a salt, a base, and acids such as an organic acid and an inorganic acid.

In various embodiments, the electrolyte is a salt. For example, the salt may be an inorganic salt. An inorganic salt may be formed from the neutralization reaction of an acid and a base. The inorganic salt may dissociate in the aqueous solution to form an ionic aqueous reagent. For example, KCl may dissociate in water to form a cation of K^+ and an anion of Cl^- . Other examples of inorganic salts include, but are not limited to $LiClO_4$, NaCl, $CaCl_2$, $BaCl_2$, $MgCl_2$, NaBr, KBr, NaI, KBr, $NaNO_3$, KNO_3 , $Mg(NO_3)_2$, $Ca(NO_3)_2$, Na_2SO_4 , K_2SO_4 , $NaClO_4$, NH_4Cl , NH_4NO_3 , $(NH_4)_2SO_4$, CH_3COONa , CH_3COONH_4 , to name only a few. At least one type of salt can be added. When two or more salts are added, they may be different types. For example, Na_2SO_4 may be added with NaCl.

The electrolyte may be a base. Non-limiting examples of a base include potassium carbonate, calcium carbonate, sodium carbonate, barium carbonate, zinc carbonate hydroxide hydrate, magnesium carbonate hydroxide hydrate, calcium hydroxide, sodium hydroxide, magnesium hydroxide and aluminum hydroxide.

In various embodiments, the electrolyte is an acid. The acid may be an organic acid or an inorganic acid. Non-limiting examples of an organic acid include carboxylic acids, sulphonic acids such as butanesulphonic acid, butanedisulphonic acid, benzenesulphonic acid,

methylbenzenesulphonic acid, ethylbenzenesulphonic acid, dodecylbenzenesulphonic acid, 2,4,6-trimethylbenzenesulphonic acid, 2,4-dimethylbenzenesulphonic acid, 5-sulphosalicylic acid, 1-sulphonaphthalene, 2-sulphonaphthalene, hexanesulphonic acid, octanesulphonic acid and dodecanesulphonic acid, and amino acids such as glycine, alanine, valine, α -aminobutyric acid, γ -aminobutyric acid, alanine, taurine, serine, ϵ -amino-nhexanoic acid, leucine, norleucine and phenylalanine.

Non-limiting examples of an inorganic acid include hydrochloric acid, sulfuric acid, sulfurous acid, nitric acid, nitrous acid, phosphoric acid, boric acid, and carbonic acid.

In various embodiments, the electrolyte is a strong acid. In specific embodiments, the acid comprises or consists of sulfuric acid.

Through present methods, a free-standing electrochromic film can be produced. This demonstrates that a single sheet of highly robust film containing all components of an electrochromic device can be produced.

The above discussion relates to a single electrode transparent conducting polymeric film with embedded electrochromic material. The above method may be extended to form a double electrode transparent conducting polymeric film whereby two opposing major surfaces of the polymeric film are conducting.

Thus, according to various embodiments, there is disclosed a method for forming a transparent conducting polymeric film, wherein the transparent conducting polymeric film comprises conductive elements and electrochromic materials embedded therein. The method includes:

applying a wetting agent/surfactant onto a first substrate;

depositing a first layer of conductive elements onto a first substrate;

depositing a first layer of electrochromic material or ion storage material onto the first layer of conductive elements on the first substrate;

depositing a first layer of polymeric material onto the first layer of electrochromic material or ion storage material;

applying a wetting agent/surfactant onto a second substrate;

depositing a second layer of conductive elements onto a second substrate;

depositing a second layer of electrochromic material or ion storage material onto the second layer of conductive elements on the second substrate;

depositing a second layer of polymeric material onto the second layer of electrochromic material or ion storage material;

positioning the first and second substrates such that the conductive elements of the first and second layers are aligned, wherein the first layer of polymeric material contacts the second layer of polymeric material;

curing the first and second layers of polymeric material to form a two-electrode transparent conducting polymeric film with embedded electrochromic material; and

peeling the transparent conducting polymeric film from the substrate.

The method of the first aspect may be further extended to form electronic devices other than electrochromic devices.

Thus, according to various embodiments, there is disclosed a method for forming a transparent conducting polymeric film, wherein the transparent conducting polymeric film comprises

conductive elements embedded therein. In such a case, the method does not include depositing a layer of electrochromic material in any of the steps. The method thus includes:

- applying a wetting agent/surfactant onto a substrate;
- depositing a first layer of conductive elements onto a first substrate;
- depositing a first layer of polymeric material onto the first layer of conductive elements;
- curing the first layer of polymeric material to form the transparent conducting polymeric film; and
- peeling off the transparent conducting polymeric film from the substrate.

To form a double electrode transparent conducting polymeric film whereby two opposing major surfaces of the polymeric film are conducting, the above method further includes depositing a second layer of conductive elements onto the first layer of polymeric material such that the first layer of polymeric material is sandwiched between the first and second layers of conductive elements prior to the curing step.

For brevity and convenience, it is to be understood that discussion on various technical features of the various methods apply equally to each other and are not repeated herein.

In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

EXAMPLES

Example 1

In this example, a step-by-step methodology according to the first aspect to fabricate a fully flexible electrochromic device based on transparent conducting grids made up of self-assembled silver nanoparticles is described. In the electrochromic device thus-formed, the electrochromic material can be embedded in the polymeric matrix with the metallic grids in addition to the subsequent deposition of the electrochromic material on top of the working electrode. A complementary electrochromic material (anodic) can also be embedded/deposited on the counter electrode.

Step 1: The substrate (in this case polyethylene terephthalate) is cleaned with ethanol and subsequently treated by oxygen plasma and/or coated with a thin layer of surfactant/wetting agent to make it hydrophilic.

Step 2: A conductive ink (in this case composed of silver nanoparticles) is drop-casted onto a stainless steel mask composed of regular array of square grids formed by stainless steel wire laying on top of a substrate as illustrated in Fig. 1A.

Step 3: The silver ink is allowed to dry in ambient environment before the stainless steel mask is removed from the substrate. Subsequently, the grid composed of silver nanoparticles is exposed to acid vapor (in this case HCl) to remove its non-conducting ligands on the nanoparticles and allow it to self-assemble and coalesce together to form conducting grids as illustrated in Fig. 1B.

Step 4: Subsequently, an electrochromic material (in this case WO_3) was deposited onto the silver grid by drop-casting or inkjet printed (or any other method) as illustrated in Fig. 1C. This will form the working electrode of the electrochromic device.

Step 5: After that, a polymer matrix that does not adhere to the substrate (in this case PVA/PMMA commercial blend or PVDF) is roll-coated onto the substrate and heated on a hotplate just below its glass transition temperature of the substrate to allow the polymer matrix to cure as illustrated in Fig. 1D. Fig. 1E shows the cross-sectional schematics at this stage.

Step 6: After the PVDF layer has cured/crosslinked, the film is peeled off, thereby exposing the conducting grids composed of Ag nanoparticles that were previously in contact with the substrate as illustrated in Fig. 1F. It is noted that the thickness of the polymer matrix can be controlled by a suitable deposition method such that both sides of the peeled PVDF film is conducting. At this stage, the electrochromic material can be further deposited on the PVDF film to achieve a higher contrast, as desired. The film at this stage is flexible and remains conductive, even when folded.

Example 2

In this example, a step-by-step methodology to fabricate a free-standing electrochromic device with all components (including working and counter electrode) embedded within the polymeric film is described, which is an extension of the first aspect of the invention.

Steps 1-4 of Example 2 are identical to Steps 1-4 of Example 1.

Step 5: Step 4 was repeated in which, a complementary electrochromic material/ion-storage material was deposited on another separate silver grid layer. This will form the counter electrode of the electrochromic device. Following that, a polymer matrix, PVDF, is roll-coated

onto both substrates as illustrated in Fig. 2A. Fig. 2B shows the cross-sectional schematics at this stage.

Step 6: Both substrates are aligned and sandwiched together with the uncured PVDF layer facing each other as illustrated in Fig. 2C.

Step 7: The sample is then placed on the oven at 85 °C for about 5 to 15 minutes to allow the polymer matrix to cure. After the PVDF polymeric matrix has cured, the PET substrate is peeled off and the film structure at this point is illustrated in Fig. 2D.

Step 8: The film is then soaked in the electrolyte overnight to allow the electrolyte to seep through/accumulate in the film. Subsequently, the film is sealed to prevent the electrolyte from drying out by a lamination/sealing process and thus completes the free-standing two-electrode electrochromic film device fabrication.

Following the same methodology above, a double-sided conducting transparent conducting film can be produced by skipping the electrochromic/ion-storage material deposition step.

Alternatively, a transparent conducting film on both sides can be formed by limiting the polymeric matrix thickness such that it does not exceed the height of the silver grid thickness as illustrated in Fig. 2E.

The advantage of using PVDF film is that the above device structure can be turned into piezochromic device, in which the device can change color upon the application of pressure.

This can be achieved by converting the alpha-phase of the non-piezochromic PVDF film into the piezochromic beta-phase PVDF film through heat treatment and/or poling process.

After the beta-phase conversion, charge can be generated when pressure is applied to the film. The charge generated can then be used to induce color change in the electrochromic device through the electrochemical redox reaction to generate and display stable and reversible color change. Through the embedded silver grid network, the charge can be applied uniformly throughout the film to produce a uniform reversible color changes.

Though this concept, a self-powered electrochromic device and/or interactive electrochromic display can be produced. In addition, this concept distinguish us clearly from any of the prior art because none of the prior art describes a transmissive piezochromic film that contains all components of an electrochromic device that will enable the film to switch colored to transparent state.

The application of piezochromics is very versatile, it can be used as a self-powered smart glass. The color switching of the glass can be activated by touching or pressing, without the need for battery or electrical supply or solar powered. In addition, it is interesting for advertising display on window or touch panel, without the need of power supply installation. With this technology, it is possible to have colored changes on paper, activated by pressing, touching or shearing.

Quantitative Proof-of-Concept

Quantitative proof-of-concept of that the fabricated film is able to switch color electrochromically in a 3-electrode setup in 1M H₂SO₄ electrolyte is shown in the UV-Vis spectra (Fig. 2G). The film is made up of the conducting silver grids with one printed layer of WO₃ (with 300 dpi

resolution). The transmission of the film with only the Ag grid (without the WO₃ layer) is about 45%. The contrast (ΔT) is about 20% at 633 nm wavelength at -1.2 V bias.

Example 3

The synthesis of silver nanoparticles can be made following the published method by S. Magdassi et al (ACS Nano 4, 2010, 1943) or Desireddy et al Nature 2013, DOI: 10.1038/nature12523). The synthesized nanoparticles concentration were adjusted to above 10 wt% in order to strike a good balance between conductivity and transparency. The conducting silver grids were first formed on pre-treated PET substrate (by plasma treatment or surfactant coating). A small amount of silver nanoparticles (between 100 to 500 μ l) is pipetted out onto a physical stainless steel mesh, which lies on top of the substrate. After the silver ink has dried, the formed grid is first exposed to fuming HCl in order to remove the polyacrylic acid polymer stabilizer and promote the self assembly of silver nanoparticles. The formed silver grid is shown in Fig. 3A.

The formed conducting Ag grid has a typical sheet resistance of between 1 and 10 $\Omega/\square$ and is approximately 5 μ m in height.

A polymer matrix (illustrated here PVA/PMMA commercial composite) is roll-coated onto the conducting silver grid and then heated at 90 °C until a film is formed. The film is then peeled off from the PET substrate, which then forms a fully flexible conducting electrode. Alternatively, a delaminating solution can be used to assist in a complete release. For example, for PVDF matrix, a delaminating solution of distilled water and acetone in the ratio of 1:1 volume ratio can be used to peel the film off the substrate easily.

Fig. 3B and 3C show the released free Ag grid embedded onto a PVA/PMMA polymer matrix. This grid has a transparency of over 70 % for most of the visible spectrum of 400 to 900 nm wavelength, which met the requirement for use in automotive windsreen requirement (requirement is over 70 % transmission), which is clearly reflected in the UV-VIS spectra shown in 3D. Optical microscopy (50x) micrograph (Fig. 3E) revealed that the Ag grids maintained its structure in its polymer matrix after the transfer. This is critical to the conductivity of the flexible polymer film.

Fabricated Devices

In order to demonstrate the functionality of the produced polymer film, the film is used in a quasi-solid state two electrode electrochromic device assembly. The schematic illustration of the electrochromic device is shown in Fig. 3F. It is worth-noting that the active electrochromic material itself can be integrated with the working electrode layer. In a prototype, the electrochromic active material PEDOT:PSS is embedded in the PDVF polymer matrix composed of conducting Ag grids (working electrode). The gel electrolyte composed of PVA/PDMS polymer mixture with LiClO_4 in PC and a PVDF separator. The working and counter electrode in the prototype is composed of the conducting Ag grids.

Upon the application of negative or positive voltage bias, the active electrochromic device is able to change its characteristic colour when it is undergoing redox reactions due to ion intercalation/deintercalation. Fig. 3G shows the coloured state and the subsequent bleaching state (Fig. 3H) of the two-electrode electrochromic device upon the application of a small voltage bias in the present free-standing two-electrode electrochromic device prototype.

The advantages of the embedded metallic grid in polymer matrix as transparent electrodes (TCs) are:

1. Compared to those with Ag structures on the surface of polymer substrate, which often encounter physical adhesion issues, prone to scratch/defects and oxidation issues, the present embedded TCs provide robust physical integrity, resistant to scratch, fully flexible, and reduce oxidation of the metallic constituent.
2. The embedded TCs are also electrochemically stable compared to those exposed metallic features that often undergo oxidation or reduction readily in an electrochemical active environment. Having the polymer matrix passivating effect, the metallic features are stable within the matrix.
3. It prevents dissolution or peeling of the metallic structures from the transparent substrate, which often leads to degraded conductivity.
4. The surface is smooth and flat compared to those with Ag structures on the surface of the substrate. This flat surface of the product created is highly desirable for the subsequent coatings for device fabrication.
5. The TC can be applied on curved surfaces and acute joints.
6. The methodology is not only limited to just metallic grids; it is also possible to be applied to other materials such as 2D nanomaterials, metallic nanowires, graphene, etc.

The piezoelectric nature of the PVDF matrix can be further developed, and it is envisioned that the free-standing two-electrode electrochromic films can respond to physical/mechanical interaction and stimulation. This can potentially be developed into novel display with high potential market in the gaming, security, and/or self-powered display sector. The application of pressure at the two ends translated into physical compression of the PVDF films, which in turn causes generation of positive charge and eventually bleaches the cathodic electroactive

electrochromic film. This effect is termed as piezochromics which translate colour changes upon mechanical or pressure stimulation, without the need of external voltage. This is a great step towards autonomous and battery-free smart windows or interactive display applications.

Example 4

Double-sided conductive transparent conducting polymer

In this example, two methods in which, a double-sided transparent conducting polymer can be realized, are illustrated.

Grid-wire structure

A polymeric matrix, for example, polyvinyl difluoride (PVDF), is roll-coated onto the metallic grid substrate (composed of nanoparticles) as illustrated in Fig. 4A. Fig. 4B shows the cross sectional schematics at this stage.

Following that, a network of Ag nanowires (NW) are spray coated onto the PVDF polymer matrix before it is cured on the hotplate (Fig. 4C). The amount of the Ag nanowire sprayed will depend on the required conductivity.

The sample is then cured on the hotplate at 85 °C to allow the PVDF polymer to cure and crosslink. Finally the PVDF film is peeled off from the substrate to form a two-sided conductive polymer film as illustrated in Fig. 4D.

Wire-wire structure

The substrate is cleaned with ethanol and subsequently treated by oxygen plasma and/or coated with a thin layer of wetting agent/surfactant to make it hydrophilic. Alternatively, BYK

348/333 (0.5 to 5 wt.%) can be applied to the substrate to make the substrate more hydrophilic and assist in the lift-off process.

Ag NW network is spray-coated (or applied using any other method such as roll-coating) onto the substrate to the desired conductivity and transparency as illustrated in Fig. 4E.

A polymeric matrix such as PVDF is then roll-coated onto the sample as shown in Fig. 4F.

Another layer of Ag NW network was deposited onto the uncured polymer matrix. The amount sprayed would depend on the desired conductivity and transparency. This step is illustrated in Fig. 4G.

The PVDF is then allowed to cure/crosslink on a hotplate or oven at 85 °C for about 5 to 10 minutes. Finally the cured PVDF film is peeled off from the substrate to form a double-sided conductive polymer film as shown in Fig. 4H.

One distinct advantage of having a grid-wire or wire-wire structure as compared to grid-grid structure is the elimination of the moiré effect that is noticeable when grid-grid structure is used due to the overlapping of similar patterns. The Ag NW network is random in nature thus preventing the moiré effect.

Example 5

Lifting-off Organic Electrochromic Material

Apart from inorganic based electrochromic material such as WO_3 , organic based electrochromic material such as PEDOT:PSS (Sigma Aldrich 483095) can also be lifted off and embedded

along with the conducting silver grids by using present methodology. The cross-section of the fabricated sample is shown in Fig. 5A.

In this sample, the PEDOT-PSS layer was drop-casted onto the Ag-grid. The UV-Visible spectra were then measured in a 3-electrode setup with Pt wire as the counter electrode and Ag wire as the reference electrode. The PEDOT:PSS could be deposited using drop casting or inkjet printing. The electrolyte used for the measurement was 1M LiClO₄ in PC. The UV-Vis spectra shown in Fig. 5B showed the initial and colored state of the film with the application of -0.9 V bias to color the film. The initial state of the film (grid + PEDOT:PSS layer) gives a transmission of about 50% at 599 nm wavelength. At the colored state (by applying -0.9 V bias), the transmission drops to 12% at 599 nm wavelength giving a contrast of 38% at 599 nm wavelength. The film can be subsequently bleached to the initial state by applying bias of about 0.2 V. There is only a variation of about 1 to 2% in transmittance of the bleached state as compared to the initial state.

Dynamic optical transmittance measurement shown in Fig. 5C also revealed that the film coloration switching speed is about 2 seconds while the bleaching speed is about 10 seconds.

Subsequent dynamic optical transmittance tests revealed that the PVDF film with embedded PEDOT:PSS (electrochromic active material) and Ag-grid is stable for at least 500 cycles with only about 5% decrease in contrast (refer Fig. 5D).

Example 6

Tuning of the transparency in the conducting polymer film

The transparency of the conducting polymer film is directly related to the size of openings of the metallic grid before lift-off. Fig. 6 shows the UV-Visible spectra of the grids with two different openings, 80 μm and 100 μm . It can be clearly observed that the grids with the larger opening (100 μm) has a higher transmittance of 75% compared to the 80 μm opening with 66% transmittance taken with respect to air. As such, the transparency in the resultant transparent conducting film can be tuned by careful selection of grid openings/windows.

In addition, apart from metallic silver grids composed of silver nanoparticles, present methodology can also lift-off/embed silver nanowires in the polymer matrix. This provides additional avenue to fine-tune the transparency of the transparent conducting film. The transparent conducting polymer film can be composed of purely metallic nanowire network or a combination of metallic-grid and nanowires. The use of nanowire allow seven larger metallic-grid openings that will be interconnected by the nanowire network. This will translate to a higher transparency without sacrificing the conductivity of the conducting polymer film.

By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for

example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

By "about" in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10% of the specified value.

The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

CLAIMS

1. A method for forming a transparent conducting polymeric film, wherein the transparent conducting polymeric film comprises conductive elements embedded therein, the method comprising:

depositing a first layer of conductive elements onto a first substrate;

depositing a first layer of polymeric material onto the first layer of conductive elements;

depositing a second layer of conductive elements onto a second substrate;

depositing a second layer of polymeric material onto the second layer of conductive elements;

positioning the first and second substrates such that the conductive elements of the first and second layers are aligned, wherein the first layer of polymeric material contacts the second layer of polymeric material; and

curing the first and second layers of polymeric material to form a two-electrode transparent conducting polymeric film.

2. The method of claim 1, further comprising:

prior to said depositing of the first layer of polymeric material, depositing a first layer of electrochromic material or ion storage material onto the first layer of conductive elements such that the first layer of electrochromic material or ion storage material is sandwiched between the first layer of conductive elements and the first layer of polymeric material.

3. The method of claim 1 or 2, further comprising:

prior to said depositing of the second layer of polymeric material, depositing a second layer of electrochromic material or ion storage material onto the second layer of conductive elements such that the second layer of

electrochromic material or ion storage material is sandwiched between the second layer of conductive elements and the second layer of polymeric material.

4. The method of any one of claims 1-3, further comprising:
prior to said depositing of the first or second layer of conductive elements, applying a wetting agent/surfactant onto at least one of the first and second substrates.
5. The method of any one of claims 1-4, further comprising removing at least one of the substrates after curing.
6. The method of claim 5, wherein removing at least one of the substrates comprises peeling off at least one of the substrates from the transparent conducting polymeric film.
7. The method of any one of claims 1-6, further comprising immersing the transparent conducting polymeric film in an electrolyte.
8. The method of any one of claims 1-7, wherein at least one of the first layer of conductive elements and the second layer of conductive elements comprises a patterned array of grids.
9. The method of any one of claims 1-8, wherein at least one of the first layer of conductive elements and the second layer of conductive elements comprises a network of nanowires.
10. The method of any one of claims 1-9, wherein at least one of the substrates comprises polyethylene terephthalate (PET) or glass.
11. The method of any one of claims 1-10, wherein at least one of the first layer of conductive elements and the second layer of conductive elements comprises conductive nanoparticles, conductive nanowires, conductive nanotubes, or conductive nanosheets.
12. The method of claim 11, wherein at least one of the first layer of conductive elements and the second layer of conductive elements comprises metallic or alloyed nanoparticles.

13. The method of claim 12, wherein at least one of the first layer of conductive elements and the second layer of conductive elements comprises silver nanoparticles, gold nanoparticles, or copper nanoparticles.
14. The method of claim 2 or claim 3, wherein at least one of the first and second layers of electrochromic material or ion storage material comprises tungsten (VI) oxide (WO_3) or poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS).
15. The method of any one of claims 1-14, wherein at least one of the first and second layers of polymeric material comprises polyvinyl alcohol (PVA), polyvinylidene fluoride (PVDF), polymethylmethacrylate (PMMA), polydimethylsiloxane (PDMS), poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), poly(3,4-ethylenedioxythiophene) PEDOT, or polyaniline (PANI).
16. The method of claim 15, wherein at least one of the first and second layers of polymeric material comprises PVDF or a mixture of PVA and PMMA.
17. The method of any one of claims 1-16, wherein depositing the first layer of conductive elements or depositing the second layer of conductive elements comprises drop-casting conductive elements to form the first layer of conductive elements or the second layer of conductive elements.
18. The method of claim 2 or claim 3, wherein depositing at least one of the first and second layers of electrochromic material or ion storage material comprises drop-casting or ink-jet printing at least one of the first and second layers of electrochromic material or ion storage material.
19. The method of any one of claims 1-18, wherein depositing at least one of the first and second layers of polymeric material comprises roll-coating at least one of the first and second layers of polymeric material.