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Photodeposition of metal oxides for electrochromic devices

Abstract

The present invention provides scalable, solution based processes for manufacturing electrochromic materials comprising metal oxide films for use in electrochromic devices. The electrochromic material comprises a transparent conductive substrate coated with an electrochromic metal oxide film, wherein the metal oxide film is formed by a process comprising the steps of: a) providing the conductive substrate; b) coating the substrate with a solution of one or more metal precursors; and c) exposing the coated substrate to near-infrared radiation, UV radiation and/or ozone in an aerobic atmosphere. The present invention also provides electrochromic devices incorporating these electrochromic materials.

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Background/Summary

CROSS-REFERENCE TO RELATED APPLICATIONS (1) This application is a national stage application under 35 U.S.C. § 371 of International Application No. PCT/CA2018/050885, filed Jul. 20, 2018, which claims the benefit of priority from U.S. Provisional Application No. 62/534,785, filed Jul. 20, 2017. The disclosures of all of the above applications are incorporated by reference herein in their entireties.

FIELD OF INVENTION
(1) The present invention relates to electrochromic films. More particularly, the present invention relates to processes for fabricating electrochromic metal oxide films for use in electrochromic

devices.

BACKGROUND

(2) Heating, ventilating, and air conditioning (HVAC) of buildings account for 30-40% of global primary energy consumption. Altering the optical and thermal properties of windows can reduce the energy deficit of a building by up to 40%. It is therefore imperative to develop technologies to dynamically adjust the transmittance of windows to reduce the energy consumption of buildings, as the ability to dynamically control window opacity to sunlight can provide the opportunity to reduce energy consumption by 20% and lighting costs by up to 50% for commercial buildings.

(3) Electrochromic windows (also known as smart or dynamic windows) undergo changes in light transmittance in response to an applied voltage, enabling dynamic control of the daylight and solar heat passing through buildings. Hence, this technology can provide indoor thermal and visual comfort for building occupants and also improve building energy efficiency. This energy-conservation technology has gained tremendous attention in industry, and in recent years, some glass companies have raised over 1 billion dollars to commercial electrochromic technology. Although large capital and efforts has been invested into this technology, the high price of electrochromic windows on the market has prevented its widespread adoption as a building material.

(4) A typical electrochromic (EC) device has a multilayer architecture consisting of active electrochromic layer, electrolyte layer, ion storage layer (counter electrode) layer, transparent conductors and supporting substrates. Among these layers, electrochromic and ion storage layers are the key components contributing to the reversible color switching. Metal oxide layers may be employed as the active electrochromic layer and/or in the ion storage layer. The most well-known electrochromic material coating used in the active electrochromic layer is WO.sub.3, which can switch reversibly and persistently between dark blue and colorless states during the operation of the device.

(5) Generating electrochromic metal oxide layers is therefore a critical step in the manufacture of electrochromic cells. Sputtering is the most common technique used today to generate these electrochromic films, but this method requires vacuum and high temperatures energy to operate. Alternative techniques that have been tried to make these layers include evaporation, chemical vapour deposition, electrodeposition, sol-gel techniques, laser ablation, sputtering and thermal deposition, but drawbacks such as cost, scalability, and obtaining the desired compositions have prevented these techniques from replacing sputtering as the industry standard.

(6) There is therefore a clear need for an alternative metal-oxide deposition process to the existing, onerous and expensive sputtering techniques that are commonly used to produce the electrochromic or light absorbing films.

SUMMARY OF INVENTION

(7) An object of the present invention is to provide scalable, solution based processes for the photodeposition of metal oxides for use in electrochromic devices. In accordance with an aspect of the present invention, there is provided an electrochromic material for use in an electrochromic device, the electrochromic material comprising a transparent conductive substrate coated with an electrochromic metal oxide film, wherein the metal oxide film is formed by a process comprising the steps of: a) providing the conductive substrate; b) coating the substrate with a solution of one or more metal precursors; and c) exposing the coated substrate to near-infrared radiation, UV radiation and/or ozone in an aerobic atmosphere to convert the one or more metal precursors to the metal oxide film on the conductive substrate, thereby forming the electrochromic material.

(8) In accordance with another aspect of the present invention, there is provided an electrochromic device comprising: (a) a first electrode comprising an electrochromic material prepared in accordance with the present methods, (b) a counter electrode, and (c) an ion-conductor layer for conducting ions between said first electrode and the counter electrode.

Description

BRIEF DESCRIPTION OF THE FIGURES

(1) FIG. **1** is a schematic depiction of an electrochromic cell and its components.

(2) FIG. **2** depicts infrared spectra monitoring the decomposition of a nickel precursor into nickel oxide in accordance with a method of the present invention.

(3) FIG. **3** depicts cyclic voltammograms of nickel oxide prepared by UV photodecomposition and NIRDD methods in accordance with the present invention.

(4) FIG. **4***a* is a schematic depiction of the formation of the amorphous tungsten oxide films by solution depositing ethanolic solutions of WCl.sub.6 on FTO glass followed by UV irradiation in accordance with the present invention.

(5) FIGS. **4***b-e* depict the result of characterizing an amorphous tungsten oxide films prepared in accordance with the present invention, including (b) XRF analysis to determine chlorine content for WCl.sub.6 on FTO glass, (c) and (d) XPS analysis of the metal oxide films on FTO glass, and (e) IR spectra of WCl.sub.3 film of FTO glass before photolysis (fresh), after UV irradiation, and after annealing step.

(6) FIG. **5** depicts electron micrographs of a-WO.sub.3 films prepared in accordance with an embodiment of the present invention.

(7) FIG. **6** depicts XRD diffractograms of a thin film of WO.sub.3 on FTO glass annealed at progressively higher temperatures up to 600° C., prepared in accordance with an embodiment of the present invention.

(8) FIG. **7** depicts transmittance data for the bleached and coloured states of a tungsten oxide film prepared in accordance with an embodiment of the present invention.

(9) FIG. **8** depicts data relating to the electrochromic properties of amorphous and crystalline WO.sub.3 prepared in accordance with an embodiment of the present invention.

(10) FIG. **9** depicts transmittance data for the bleached and coloured states of nickel oxide prepared in accordance with an embodiment of the present invention.

(11) FIG. **10** is a plot depicting voltage cycling and stability over 100 cycles of nickel oxide films prepared in accordance with an embodiment of the present invention.

(12) FIG. **11** depicts cycling voltammograms of nickel oxide films prepared in accordance with an embodiment of the present invention over in aqueous (H.sub.2O) and non-aqueous solvents (PC—propylene carbonate).

(13) FIG. **12** depicts transmittance data for nickel oxide and lithium nickel oxide films prepared in accordance with an embodiment of the present invention during cycling events.

(14) FIG. **13** depicts data relating to the characterization of an amorphous vanadium oxide film prepared in accordance with an embodiment of the present invention, including (a) XRF analysis to determine chlorine content for VCl.sub.3 on FTO glass, (b) and (c) XPS analysis of the metal oxide films on FTO glass, and (d) IR spectra of VCl.sub.3 film of FTO glass before photolysis (fresh), after UV irradiation, and after annealing step.

(15) FIG. **14** depicts transmittance data for the bleached and colored states of vanadium oxide film prepared in accordance with an embodiment of the present invention.

(16) FIG. **15** depicts data relating to the characterization of an amorphous niobium oxide film prepared in accordance with an embodiment of the present invention, including (a) XRF analysis to determine chlorine content for NbCl.sub.5 on FTO glass, (b) and (c) XPS analysis of the metal oxide films on FTO glass, and (d) IR spectra of NbCl.sub.5 film of FTO glass before photolysis (fresh), after UV irradiation, and after annealing step.

(17) FIG. **16** depicts transmittance data for the bleached and colored states of niobium oxide film prepared in accordance with an embodiment of the present invention.

(18) FIG. **17** depicts data relating to the characterization of an amorphous molybdenum oxide film

prepared in accordance with an embodiment of the present invention, including (a) XRF analysis to determine chlorine content for $MoCl_5$ on FTO glass, (b) and (c) XPS analysis of the metal oxide films on FTO glass, and (d) IR spectra of $MoCl_5$ film of FTO glass before photolysis (fresh), after UV irradiation, and after annealing step.
(19) FIG. **18** depicts transmittance data for the bleached and coloured states of molybdenum oxide film prepared in accordance with an embodiment of the present invention.
(20) FIG. **19** depicts data relating to the determination of ΔT, $t_{b,90\%}$, and $t_{c,90\%}$ and CE of devices assembled with: (a) as-prepared WO_3; (b) WO_3 annealed at 200° C. in air for 1 hr; and (c) WO_3 annealed at 600° C. in air for 1 hr.
(21) FIG. **20***a* depicts data relating to the optical transmittance spectra for electrochromic devices containing V_2O_5, Nb_2O_5, or MoO_3 active layers, prepared in accordance with the present invention, (each annealed at 100° C.) in the colored and bleached states formed at the indicated potentials.
(22) FIG. **20***b* depicts data relating to the change in Δ(OD) as a function of charge density for electrochromic devices containing V_2O_5, Nb_2O_5, or MoO_3 active layers, prepared in accordance with the present invention.
(23) FIG. **21***a* is a schematic depiction of the formation of the amorphous nickel oxide films by solution depositing ethanolic solutions of $NiCl_2$ on FTO glass followed by UV irradiation in accordance with the present invention.
(24) FIGS. **21***b-d* depicts the results of characterizing the NiO_x films prepared in accordance with the present invention, including (b) XRF analysis to determine chlorine content as a function of time, (c) and (d) XPS analysis of the metal oxide film on FTO glass.
(25) FIG. **22***a* is a schematic depiction of the architecture of a solid state EC device using an NiO_x film on the FTO glass counter electrode as an ion storage material, prepared in accordance with an embodiment of the present invention.
(26) FIGS. **22***b-d* depict the results of characterizing solid state devices employing an NiOx film on the counter electrode prepared in accordance with an embodiment of the present invention, including (b) a comparison of the transmittance spectra obtained for EC devices prepared with and without a-NiO_x on the FTO glass counter electrode, (c) the transmittance change for the EC device prepared with a-NiO_x on FTO as counter electrode as a function of time, and (d) changes in optical density at 633 nm as a function of charge density for a solid state EC device prepared using a-NiO_x on the FTO glass counter electrode.
(27) FIG. **23** depict the result of characterizing and comparing performances of EC devices using amorphous and crystalline nickel oxides as counter electrodes, prepared in accordance with an embodiment of the present invention FIG. **24***a* is a schematic depiction of a device employing a TiO_2 film on the FTO glass counter electrode as an ion storage material, prepared in accordance with an embodiment of the present invention.
(28) FIG. **24***b* depict the results of characterizing and comparing EC devices employing a TiO_2 film on the FTO glass counter electrode as an ion storage material, including (b) maximum and minimum transmittance at wavelength of 700 nm over 1000 cycles for EC devices with WO_3 as the electrochromic layer, and a-TiO_2 (light grey) or crystalline c-TiO_2 (dark grey) deposited on FTO as the counter electrode, or without a TiOx film.
(29) FIG. **25** depicts the results of characterizing WO_3 films of difference thicknesses prepared in accordance with the present invention.
(30) FIG. **26** depicts transmittance data for a WO_3 film on tin-doped indium oxide (ITO) coated polyethylene terephthalate (PET), prepared in accordance with the present invention.
(31) FIG. **27** depicts transmittance data for undoped WO_3 and Nb-doped WO_3 films on FTO glass, prepared in accordance with the present invention.
(32) FIG. **28**, depicts transmittance data for undoped WO_3 and Ti-doped WO_3 films on FTO glass prepared in accordance with the present invention

DETAILED DESCRIPTION OF THE INVENTION

Definitions

(33) "Amorphous" means a chemical composition without long-range order in its atomic structure.

(34) "Electrochromic cell" refers to a cell that is capable of transitioning transparency from a colored state (i.e., low transmittance of light through the window) to a transparent state (i.e., high transmittance of light through the window), and/or from a transparent state to a colored state, through the use of an applied electrical bias. The "transparent" state may also be referred to as a "bleached" state.

(35) "Ligand" means any chemical group coordinated, chemically bonded or ionically bonded to a metal. Typical ligand examples are, but not limited to, chloride, bromide, nitrate, 2-ethylhexanoate and acetylacetonate.

(36) "Metal Oxide" may refer herein to any single solid containing a metal and oxygen, where the ratio of metal to oxygen is undefined and therefore represented as MO.sub.x. Examples of single metal oxides that may be suitable for use as an electrochromic material include, but are not limited to, NiO.sub.x, WO.sub.3, MoO.sub.3, TiO.sub.2, Ta.sub.2O.sub.5, V.sub.2O.sub.5, Nb.sub.2O.sub.5, COO.sub.2, MnO.sub.2, and FeO.sub.x.

(37) "Mixed Metal Oxide" refers to a film that contains at least two metals and is an oxide. Examples of mixed metal oxides that may be suitable for use as an electrochromic material include, but are not limited to, LiNiO.sub.x, TiWO.sub.x, and FeNiO.sub.x.

(38) "Metal Precursor" describes any chemical containing a metal that is deposited onto a substrate and then converted into a metal oxide. Typical examples include, but are not limited to, metal chloride, metal 2-ethylhexanoate and metal acetylacetonate, wherein the metal may be any of the metals identified above.

(39) "Reduced Iron Oxide" refers to the compound FeO where iron and oxygen are present in nearly equal amounts.

(40) "Sputtering" refers to a technique whereby a pure metal is exposed to high energy that ejects atoms of the metal into a medium with the atoms subsequently being deposited onto a substrate.

(41) "Substrate" refers to the material upon which the metal oxide coating is assembled. The substrate material may be inherently conductive, or the conductivity may be engendered through application of a conductive film to the surface of the material. A suitable film typically comprises a transparent conductive oxide (TCO) such as fluorine tin oxide (FTO); indium tin oxide (ITO); aluminum zinc oxide (AZO) and various others. Other suitable support materials include any transparent glasses, plastics, polymers (e.g. PET), or rubbers compatible with a relevant conductive layer.

(42) This present invention relates to electrochromic devices comprising electrochromic metal oxide and/or mixed-metal oxide films produced using scalable fabrication processes which do not require a vacuum, and which may be carried out at an ambient or elevated temperature.

(43) An objective of the present invention is therefore to provide low cost, scalable, solution based processes for manufacturing an optical quality film of a metal oxide or mixed metal oxide coated on a suitable conductive substrate, for use in an electrochromic device. In accordance with the present invention, the metal oxide and/or mixed metal oxide films formed using the present processes are electrochromic, i.e., capable of transforming its transparency from the colored state to a transparent state (or transparent state to a colored state) upon the introduction of an external electrical bias.

(44) The invention further provides photochemical methods suitable for the large-scale processing and manufacturing of the desired metal oxide and mixed metal oxide films, in amorphous or crystalline phases, for use in the electrochromic devices of the present invention.

(45) The present disclosure describes two methods suitable for making metal oxides and mixed metal oxides for electrochromic devices: Near Infrared Driven Decomposition (NIRDD) or UV photodecomposition. Both NIRDD and UV photodecomposition are methods of manufacture that

operate at lower temperatures with solution processable precursors that afford precise composition control and lower cost manufacturing than existing state-of-the-art techniques.
(46) In one embodiment, there is provided a Near-Infrared Driven Decomposition (NIRDD) method, which uses infrared light to decompose a metal precursor to generate the corresponding metal oxide or mixed metal oxide, if formed in the presence of air. PCT Patent Publication No. WO2016101067 A1 describes an NIRDD method for the preparation of metal oxides and mixed-metal oxides, the entire disclosure of which is incorporated herein by reference.
(47) In one embodiment, there is provided a UV photodecomposition method, in which the metal precursor is subjected to ultraviolet radiation, optionally in the presence of ozone, to remove all ligands and produce the desired metal or mixed-metal oxides under aerobic atmosphere. UV photodecomposition operates at either ambient or elevated temperatures. U.S. Pat. No. 9,433,928 describes a UV photodecomposition technique for generating metal oxides and mixed-metal oxides for use in methods for making electrocatalysts, the entire disclosure of which is incorporated herein by reference.
(48) When carried out on a metal precursor in the absence of air, both UV photodecomposition and NIRDD can result in a more reduced phase of the corresponding metal.
(49) The electrochromic metal oxide and/or mixed-metal oxide films formed using the methods of the present invention may be amorphous or crystalline.
(50) In one embodiment of the present invention, the metal oxide or mixed metal oxide is formed on a transparent conductive oxide layer and subsequently incorporated into an electrochromic cell that is capable of transitioning from opaque to transparent or transparent to opaque through the use of an applied electrical bias.
(51) In accordance with the present invention, one or more metal or mixed metal oxide coatings are employed as layers in an electrochromic cell that are incorporated into “smart glass” applications such as electrochromic windows.
(52) The general configuration of an electrochromic device comprises an anode and cathode supported on transparent conductive substrates and an inter-electrode ion conductor (electrolyte). The anode and/or the cathode may comprise electrochromic material(s). The function of each component of the overall device is described in detail below, and a schematic depiction of the overall device architecture is presented in FIG. **1**.
(53) When a voltage is applied across the electrodes, an electric field is generated within the insulating electrochromic material, which can cause migration of ions to or from the electrochromic material producing colour changes in that electrochromic material (e.g., from bleached to colored when switched from one electrochromic state to another). By reversing the applied bias, the electrochromic material can be switched back (e.g., from colored to bleached state). The electrochromic material may also be colored initially, and switch to a colorless/bleached state with applied voltage, and then switched back to the colored state by reversing the applied bias. For example, tungsten oxide based films colour with ion insertion, whereas nickel oxide based films colour with ion extraction.
(54) The role of the electrolyte layer in an electrochromic cell is to allow ions to travel between the anode and cathode materials. An example of a common electrolyte for electrochromic devices is LiClO.sub.4 in propylene carbonate.
(55) As such, a typical electrochromic device has a multilayer architecture consisting of active electrochromic layer, electrolyte layer, ion storage layer (counter electrode) layer, transparent conductors and supporting substrates. Among these layers, electrochromic and ion storage layers are the key components contributing to the reversible color switching.
(56) A good electrochromic material exhibits a high colour contrast between its coloured and bleached states, has rapid conversion between coloured and bleached states, is capable of switching between colored and bleached at low applied voltage, shows excellent reversibility with cycling between states, and excellent stability.

(57) In accordance with preferred embodiments of the present invention, the metal oxide and mixed-metal oxide films employed in the electrochromic devices comprise NiO.sub.x, WO.sub.x, NbO.sub.x, MoO.sub.x, MnO.sub.x, CoO.sub.x, VO.sub.x, TaO.sub.x, TiO.sub.x and LiNiO.sub.x, or combinations thereof.
(58) Another application for the metal or mixed metal oxide is to provide coatings on windows that preclude the entry of long wavelength solar radiation, alone or in combination with the electrochromic metal oxide coatings. In one embodiment, the light absorbing coating is provided by a reduced iron oxide film. The reduced iron oxide may be produced by either NIRDD or UV photodecomposition in an inert atmosphere such as nitrogen or argon. In all of these embodiments, a reduced iron oxide layer may be incorporated to block near-infrared light without affecting visible light, thereby serving to absorb near-infrared wavelengths while allowing visible light to pass through.
(59) The most well-known electrochromic material coating that comprises the working electrode is WO.sub.3 film that switches reversibly and persistently between dark blue and colorless states during the operation of the device.
(60) Tungsten trioxide ("WO.sub.3") is a well known cathodic electrochromic material that cycles between a pale yellow (or transparent) neutral and deep blue reduced state in electrochromic devices. The transparent film can be electrochemically reduced in the presence of lithium ions to form the colored, reduced state ("LiWO.sub.3"), and reversibly re-oxidized to the transparent state. The methods of the present invention can be used to form WO.sub.x films for use in the electrochromic devices.
(61) Examples of other electrochromic cathodic materials include, but are not limited to, MoO.sub.3, TiO.sub.2, Ta.sub.2O.sub.5, V.sub.2O.sub.5, NiO.sub.x, and Nb.sub.2O.sub.5.
(62) Nickel oxide ("NiO.sub.x") is a known anodic electrochromic material that colours complementary to tungsten oxide to create a better colored dark state in the electrochromic cell. The methods of the present invention can be used to form NiO.sub.x films for use in the electrochromic devices.
(63) Another example of a good anodic electrochromic material is IrO.sub.2. Materials such as CoO.sub.2, MnO.sub.2 and FeO.sub.2 have also been shown to exhibit electrochromic behavior, but are not ideal as they do not bleach completely.
(64) Iron oxide ("FeO") is a material known for a high absorption of near-infrared light relative to visible light. It can be used for coatings on architectural glass to reduce interior solar heating of buildings. Thin films of FeO can be created by sputtering, or chemical vapor deposition under anoxic conditions.
(65) Transparent conductive metal oxides (TCOs) such as tin doped indium oxide (ITO) and fluorine doped tin oxide (FTO) are frequently used as counter electrodes in isolation or coated with additional ion storage materials. Although devices with bare TCO for their counter electrode usually show better transparency in the bleached state, in such devices the charge is usually not balanced between the two electrodes, which may be detrimental to the device stability. The methods of the present invention can be used to form a stabilizing metal oxide ion storage layer.
(66) A metal precursor or combination of metal precursors is/are coated onto a substrate that may include, but is not limited to, glass, plastic, composites, etc. In an embodiment of the present invention, the preferred substrate is transparent and is either glass or plastic.
(67) Coating the chosen substrate can be performed using a variety of methods including spin coating, painting, dip coating, spray coating, ultra-sonic spray coating or other methods familiar to those skilled in the art. A coating solution is prepared by dissolving the metal precursor or precursors into a compatible solvent and then applying the solution to the surface of the substrate. Upon drying, a layer of the desired precursor or precursors is formed on the substrate. Examples of compatible solvents include but are not limited to water, methanol, ethanol, isopropanol, acetone, hexane, acetylacetone, and methyl isobutyl ketone.

(68) Metal precursors suitable for use in the processes of the present invention include any metal derivative that can be converted to the corresponding metal oxide upon exposure to near-infrared radiation, UV radiation and/or ozone. Suitable precursors include, but are not limited to, metal chlorides, metal 2-ethylhexanoate and metal acetylacetonates. Exemplary embodiments of metal precursors include WCl_6, $Ni(eh)_2$, $NiCl_2$, VCl_3, $NbCl_5$, $MoCl_5$, Li(eh), $W(O\text{-}iPr)_6$ and $Ti(eh)_4$.
(69) Either the NIRDD and/or UV photodecomposition method can be used to convert the metal precursor that is coated onto the substrate to the desired amorphous or crystalline metal oxide or mixed-metal oxide in air at ambient or elevated temperature. Forming a mixed-metal oxide using the sputtering technique is comparatively more onerous.
(70) In one embodiment of the synthesis of a metal oxide film, a precursor solution is produced by dissolving the metal precursor in anhydrous ethanol. The precursor solution is then spin-coated on FTO glass, and the resultant precursor thin films are subjected to UV or NIR irradiation until decomposition is confirmed through monitoring of ligand loss using spectroscopic methods. To produce multi-layer thin films, the spin-coating and irradiation steps are repeated multiple times.
(71) In certain embodiments, the as-deposited films undergo an annealing step in an oven in air at temperatures ranging from 50-750° C. for 1 hour using a ramping rate of 10° C./min. In one embodiment, the films undergo an annealing step at 100° C. for 1 hour. In one embodiment, the films undergo an annealing step at 200° C. for 1 hour. In one embodiment, the films undergo an annealing step at 200° C. for 1 hour. In one embodiment, the films undergo an annealing step at 600° C. for 1 hour.
(72) For precursors comprising organic ligands, formation of the desired metal oxide can be monitored by infrared spectroscopy, as loss of ligands from the metal precursor gives rise to a loss of ligand signal in the infrared spectrum. FIG. **2** depicts the transformation from the nickel 2-ethylhexanoate metal precursor to amorphous nickel oxide using both the UV photodecomposition and NIRDD methods.
(73) For precursors which cannot be tracked by infrared spectroscopy, including but not limited to metal chloride salts, X-ray fluorescence (XRF) spectroscopy can be used to monitor the transformation to amorphous metal oxide.
(74) In accordance with the present invention, both the NIRDD and UV photodecomposition methods can be used to produce the same final metal oxide films. FIG. **3** depicts the cyclic voltammetry of nickel oxide films produced using both the NIRDD and UV photodecomposition methods of the present invention. Both voltammetry curves depict the same shape and features indicating that the amorphous metal oxide films generated by NIRDD and UV photodecomposition are electrochemically the same.
(75) The following performance metrics were evaluated for the devices formed using metal oxide films prepared using the methods of the present invention: (i) maximum optical modulation (ΔT), the difference of light transmittance between fully colored and bleached states; (ii) switching time for coloring ($t_{c,90\%}$) and bleaching ($t_{b,90\%}$) required to reach 90% of full change of transmittance between the respective fully colored and cleared states; and (iii) coloration efficiency (CE), which corresponds to the change in optical density (Δ(OD)) in response to the change in charge per unit area (ΔQ). The value of CE was acquired by fitting the linear region in the plot of Δ(OD) as a function of ΔQ, and extracting the slope in accordance with Eq. 1 (where T_b and T_c are the transmittance in the bleached state and colored states, respectively, at a given wavelength).
(76) $$CE = \frac{\Delta(\mathrm{OD})}{\Delta Q} = \frac{\log\left(\frac{T_b}{T_c}\right)}{\Delta Q} \quad (\text{Eq. } 1)$$
(77) In one embodiment, amorphous tungsten oxide films produced in accordance with the methods of the present invention exhibit electrochromic properties suitable for use in electrochromic devices. FIG. **4***a* is a schematic depiction of the formation of the amorphous

tungsten oxide films by solution depositing ethanolic solutions of WCl_6 on FTO glass followed by UV or NIR irradiation in accordance with the methods of the present invention.
(78) Amorphous tungsten oxide formed using NIRDD or UV photodecomposition shows broad transmittance in bleached mode (35-75%) and a reduced transmittance in colored mode (5-20%) over the entire visible spectrum as depicted in FIG. **7**. The amorphous WO_3 films demonstrated voltage-controlled light transmittance over the visible and infrared range (400-1000 nm). The transparency of the tungsten oxide film can be precisely manipulated by controlling the applied bias. Upon introduction of a positive bias the bleached state is generated and transmittance increases. Application of a negative bias generates the coloured state and light transmittance is decreased through the tungsten oxide (FIG. **7**).
(79) In one embodiment, amorphous nickel oxide films formed using the NIRDD and UV photodecomposition methods of the present invention also exhibit electrochromic properties suitable for use in electrochromic devices. Upon introduction of a positive bias, the colored state is generated and transmittance decreases. Application of a negative bias generates the bleached state and light transmittance is increased through the nickel oxide. The transparency of the nickel oxide film can be precisely manipulated by controlling the applied bias. A full spectrum transmittance curve for both bleached and colored modes of a nickel oxide film prepared in accordance with the present invention is shown in FIG. **9**. Under colored conditions the transmittance ranges from 15-45%, while in bleached mode the transmittance is between 40-70%. Amorphous nickel oxide formed by either the UV photodecomposition or NIRDD methods of the present invention exhibits long-term stability cycling between colored and transparent modes as depicted in FIG. **10**. Samples cycled over a time period of 12000 s (100 cycles) repeatedly return to within 5% of their transmittance levels after each individual cycle.
(80) The electrolyte/ion conductor between the anode and cathode materials can be modified to impart desired transparency, conductivity and durability properties. Amorphous nickel oxide films formed using the methods of the present invention provide additional flexibility for electrochromic device design by operating successfully in both aqueous and organic electrolytes. Cyclic voltammetry curves shown in FIG. **11** reveal repeatable, reversible oxidation and reduction peaks in aqueous and non-aqueous solvents demonstrating the stability of the amorphous nickel oxide layer.
(81) Mixed metal oxides have been shown in other applications (e.g. superconductors, electrolysis) to achieve superior performance with respect to individual metal oxides. This improvement in performance is achieved through synergistic and energetic effects at the atomic and nanoscale. For the present invention lithium was introduced into the amorphous nickel oxide film in a ratio of 1:3. The mixed metal oxide film $LiNi_3O_x$ achieves steady-state electrochromism much faster (by seconds) than the amorphous nickel oxide as depicted in FIG. **12**. Faster steady-state electrochromism is advantageous for commercial applications, especially those requiring rapid transitions of the electrochromic cell from opaque to transparent.
(82) The generality of the presently methods for making electrochemically active oxide layers was extended to amorphous films of V_2O_5, Nb_2O_5, and MoO_3 derived from VCl_3, $NbCl_5$, and $MoCl_5$, respectively. The electrochromic devices containing V_2O_5, Nb_2O_5, and MoO_3 each showed optical modulation in the visible range with at 20%, 30%, and 35%, respectively at wavelengths of 700 nm (FIG. **14**, **16**, **18**, respectively). Larger changes in transmittance were observed at different wavelengths. XPS analyses of each of the as-prepared oxide films confirmed the absence of chlorine and the stabilization of the respective metals (vanadium, niobium, or molybdenum) in their fully oxidized chemical states (FIGS. **13***a*, **15***a* and **17***a*, respectively). The as-prepared V_2O_5, Nb_2O_5, and MoO_3 thin films contained residual water that was effectively removed by further annealing for 1 hour at 100° C. (FIGS. **13***d*, **15***d* and **17***d*, respectively). The electrochromic devices containing V_2O_5, Nb_2O_5, and MoO_3 each showed

optical modulation in the visible range with coloration efficiencies of 36, 22, and 57 cm.sup.2/C at wavelengths of 450, 500, and 550 nm, respectively (FIG. **20**). FIG. **20***a* depicts the optical transmittance spectra for electrochromic devices containing three V.sub.2O.sub.5, five Nb.sub.2O.sub.5, or five MoO.sub.3 active layers (each annealed at 100° C.) in the colored and bleached states formed at the indicated potentials. FIG. **20***b* depicts the plots of Δ(OD) for V.sub.2O.sub.5 at 450 nm, Nb.sub.2O.sub.5 at 550 nm, and MoO.sub.3 at 550 nm as a function of charge density. The CE values obtained by fitting the linear region of each plot are also indicated in FIG. **20***b*.

(83) FeO films produced by UV decomposition and NIRDD show a strong absorbance in the near-infrared region while remaining transparent to visible light. A FeO film applied to an electrochromic device will block near infrared light regardless of the state of the device, either on or off.

(84) Table 1 compares the CE of various electrochromic metal oxides prepared via different methods. In all cases, the methods described herein provide metal oxide films that are similar, or better than, the films made by other methods.

(85) TABLE-US-00001 TABLE 1 Electrochromic performance parameters for cathodic electrochromic films. Preparation CE Wavelength.sup.a Active layer Description method (cm.sup.2/C) (nm) Ref Amorphous 600-nm amorphous film photodeposition 133 700 this work WO.sub.3 Crystalline WO.sub.3 600-nm crystalline film photodeposition 69 700 this work WO.sub.3 amorphous film electrochemical 62 630 Srivastava et deposition al. (2005) WO.sub.3•2H.sub.2O crystalline nanosheets chemical solution 121 700 Liang et al. (2013) WO.sub.3 crystalline nanowires hydrothermal 103 630 Zhang et al. (2011) WO.sub.3 crystalline mesoporous chemical 40 630 Brezesinski condensation et al. (2006) V.sub.2O.sub.5 amorphous film photodeposition 36 450 this work V.sub.2O.sub.5 crystalline electrochemical 36 430 Scherer et deposition al. (2012) V.sub.2O.sub.5 crystalline electrochemical 32 450 Tong et al. nanofibers deposition (2015) Nb.sub.2O.sub.5 amorphous photodeposition 22 500 this work Nb.sub.2O.sub.5 amorphous chemical 29 500 Llordes et al. condensation (2016) Nb.sub.2O.sub.5 amorphous thermal 15 500 Llordes et al. condensation (2016) MoO.sub.3 amorphous photodeposition 57 550 this work MoO.sub.3 amorphous chemical vapor 26 550 Maruyama et deposition al. (1995) MoO.sub.3 crystalline sol-gel 24 550 Hsu et al. nanoparticles (2008) .sup.aWavelength at which optical data for CE values were recorded.

(86) The methods of the present invention can also be used to deposit a metal oxide film as an ion storage layer on the counter electrode. Ion storage material coated on a TCO substrate can efficiently balance the charges generated by the working electrode (typically WO.sub.3) during operation by storing Li-ions during device bleaching and releasing Li-ions that intercalate into the WO.sub.3 during colouration. NiO and IrO.sub.2 are the commonly used ion storage materials in EC devices, and can improve colouration intensity by providing complementary colouration for the EC devices. However, due to the intrinsic colour of NiO and IrO.sub.2, the optical modulation value may be compromised. While is the use of an optically passive ion storage materials such as CeO.sub.2 can preserve the transparency of the device in the bleached state, its ion storage capacity is limited. It is therefore highly desirable to seek alternative optically passive counter electrode materials that also demonstrate outstanding ion storage capacity. TiO.sub.2 exhibits excellent lithium ion storage capability when used as an anode material in lithium ion batteries, indicating that TiO.sub.2 thin films can be used as ion-storage materials for application on the counter electrodes of EC devices.

(87) In one embodiment, an amorphous TiO.sub.2 film prepared in accordance with the methods of the present invention is employed as a counter electrode material for use in EC devices.

(88) In one embodiment, an ion storage metal oxide film is coupled to a photodeposited electrochromic film prepared in accordance with the present invention to form a solid state electrochromic device that shows state-of-the art electrochromic performances. Solid-state

electrochromic devices can avoid the safety and sealing issues existing in a device using liquid electrolyte.

(89) The invention will now be described with reference to specific examples. It will be understood that the following examples are intended to describe embodiments of the invention and are not intended to limit the invention in any way.

EXAMPLES

Example 1: NiO_x UV Photodecomposition

(90) In this example, fluorine-doped tin oxide (FTO; TEC 7; 7 Ω/sq) substrates are cut into 2.5 by 2.5 cm squares and cleaned with sonication in Extran® 300 detergent for 15 minutes, deionized H_2O for 15 minutes, acetone for 15 minutes, exposed to UV light with $O_{3}(g)$ for 20 minutes and spin coated. The precursor solution is a photoactive nickel compound. In this example, nickel (II) 2-ethylhexanoate (78% (w/w) in 2-ethylhexanoic acid, Strem Chemicals) was used. A 0.2 M solution in ethanol was prepared and applied to the clean FTO surface. The sample was spin-coated (3000 rpm, 60 s) to yield a thin film of nickel (II) 2-ethylhexanoate. The coated substrates were then exposed to UV radiation. In this example, the samples were placed under a dual wavelength UV lamp (I=185, 254 nm) for 24 hours. Precursor decomposition was monitored by infrared (IR) spectroscopy and was considered complete when stretches corresponding to the corresponding ligand have disappeared.

Example 2: NiO_x NIRDD

(91) In this example, the same precursors are applied to the same substrates and spin-coated in the same manner as Example 1. In this case, the samples are placed under an infrared lamp to induce precursor decomposition to form an a-NiO_x film. The films formed are transparent following decomposition. The precursor decomposition can be tracked in the same manner as in Example 1.

Example 3: Device Assembly

(92) Films prepared in accordance with the present methods (including those formed in Examples 4 to 15) were incorporated into electrochromic devices fabricated by placing a 2×2 cm square silicone rubber sheet (20 A, thickness=1 mm; McMaster-CARR) with a centered hollow circle (diameter=1.6 cm) on top of a bare FTO glass that serves as the counter electrode. FTO glass was then coated with the electrochromically active metal oxide films (working electrode) laid on top the silicon spacer to form a closed cell. Epoxy glue was used to seal three sides of the cell. A 1-M $LiClO_4$ propylene carbonate electrolyte solution was injected into the cell by a syringe through the unsealed side. Prior to injection, the empty cell and the electrolyte in a vial were purged with dry N_2 for 5 min respectively to drive away ambient air. Sealing the fourth side with epoxy glue provided the final electrochromic device. The assembled device had an active area of 2.0 cm^2.

Example 4: WO_3 UV Photodecomposition

(93) In this example, the transparent conductive oxide was prepared in the same manner as Example 1. Anhydrous ethanol is added to tungsten (VI) chloride (WCl_6, Sigma-Aldrich) to make a 0.25 M solution. This solution was stirred for 16 hours and spin-coated onto a substrate (3000 rpm, 60 s) yielding a dark blue film on the substrate. The substrate was then placed under a UV lamp (I=185 or I=185, 254 nm) for decomposition of the precursor to form a-WO_3. Transformation to the metal oxide was monitored by X-ray fluorescence. The electrochromic devices were assembled as described in Example 3, with 600-nm films of WO_3 films (corresponding to 5 sequential depositions of the tungsten precursor) on FTO glass as the working electrode. The amorphous WO_3 films in the devices (denoted as a-WO_3) were annealed at 100° C. for 1 hr prior to being placed in the device to suppress delamination from the substrate.

(94) FIG. **4***b* shows the results of the XRF monitoring of the chlorine content for WCl_6 on FTO glass as the chloride precursor decomposes during UV photodecomposition for tungsten, and confirm by XRF analysis complete decomposition of the precursor within 3 min of UV irradiation. FIGS. **4***c* and **4***d* show that the XPS analysis of the metal oxide films on FTO glass is consistent

with the formulation of WO_3 given the presence of W4f spectral signatures consistent with W^{6+}. FIG. **4***e* depicts the IR spectra of WCl_6 dissolved in ethanol spin-cast on FTO glass before and after being subjected to UV irradiation for 3 min, as well as the IR spectrum recorded on a layer of WO_3 formed after exposure to UV light for 3 min and annealed at 100° C. for 1 hr.

(95) FIG. **5** depicts the SEM, TEM, and HRTEM characterization of a single WO_3 layer prepared in accordance with the UV irradiation method of the present invention, and annealed for 1 hr at 100° C. The electron micrographs of FIG. **5** show uniform, high-porosity, amorphous films with thicknesses of 200 nm. The iridium and platinum layers shown in the cross-sectional SEM image were deposited to reduce charging effects by increasing film conductivity and to protect the underlying film from the focused ion beam used to create the cross section.

(96) The amorphous nature of the WO_3 thin films was further supported by XRD diffractograms that show no evidence of crystalline phases other than the FTO substrate (FIG. **6**). The films were annealed in 100° C. steps from 100-600° C. for 60 min each. The presence of a crystalline phase, namely monoclinic WO_3, was only detected when the films were heated above 400° C. The crystalline WO_3 films display electrochromic properties also.

Example 5: Comparison of the Electrochromic Properties of Amorphous and Crystalline WO_3

(97) The effects of annealing on amorphous WO_3 film produced in Example 4 were investigated. The benchmark crystalline film (denoted as c-WO_3) was prepared following the same protocol described in Example 4, but with an additional 1 hr annealing step at 400° C.

(98) Optical transmittance spectra of the devices under coloring and bleaching biases show that the change in transmittance value of ˜70% measured at 700 nm for the amorphous WO_3 is ˜15% higher than the values measured for the crystalline WO_3 (FIG. **8***a*). The transmittance change at 700 nm when the device is switched from colored to bleached back to colored for devices containing amorphous and crystalline films is shown in FIGS. **8***b* and **8***c*, respectively. Switching times are indicated. The switching time of coloring ($t_{c,90\%}$, defined by the time required to reach 90% of full change of transmittance from clear to colored state) (12 s) and the switching time of bleaching from colored to clear state ($t_{b,90\%}$) (5 s) values measured for amorphous WO_3 (FIG. **8***b*) were markedly faster than those for crystalline WO_3, which show $t_{c,90\%}$ and $t_{b,90\%}$ values that are 5- and 35-fold longer, respectively (FIG. **8***c*). FIG. **8***d* depicts changes in optical density (Δ(OD)) at 700 nm as a function of charge density. CE values were determined by fitting the linear region of the plot. The colouration efficiency (CE) of the amorphous WO_3 was calculated to be 133 cm^2/C at a wavelength of 700 nm, which is almost twice that of crystalline WO_3 (FIG. **8***d*). FIGS. **8***e* and **8***f* depict the transmittance change at 700 nm during the electrochromic switching between colored and bleached states for 100 cycles in 30 s steps. The stability of amorphous WO_3 (formed by either UV photodecomposition or NIRDD) over 1000 cycles of switching the applied bias from −3.5 V for 30 s to 3.0 V for 30 s confirmed that 90% of the initial transmittance change was retained (FIG. **8***e*). There is almost negligible degradation in the initial 100 cycles of the amorphous oxide (FIG. **8***e*), however, the transmittance change for the crystalline tungsten oxide showed significant degradation over the same 100 cycles (FIG. **8***f*).

Example 6: Effect of Annealing Temperature on Electrochromic Performance

(99) An amorphous WO_3 film was prepared in accordance with the method described in Example 4. The as prepared film WO_3 was further subjected to an annealing step at 200° C. and an annealing step at 600° C. (Annealing performed in air for 1 hr). The resulting films were characterized and the AT, $t_{b,90\%}$, and $t_{c,90\%}$ and CE values of devices assembled are provided in FIG. **19**: (a) as-prepared WO_3; (b) WO_3 annealed at 200° C.; and (c) WO_3 annealed at 600° C.

(100) TABLE-US-00002 TABLE 2 Performance parameters as a function of annealing

temperatures of the active layer for devices assembled with photo-deposited WO.sub.3..sup.a annealing temperature ΔT t.sub.c,90% t.sub.b,90% CE (° C.) (%) (s) (s) (cm.sup.2/C) as-prepared 60 15 4 92 100 70 12 5 133 200 66 14 6 131 400 56 68 166 69 600 42 101 109 69 .sup.aDevice active layers are ~600 nm (5 successive layers of deposition). Operational potentials for the colored and bleached forms were −3.5 and +3.0 V. Optical data was measured at 700 nm. Values for ΔT, t.sub.c,90%, t.sub.b,90% and CE are also shown in FIG. 19.

Example 7: Effect of WO.SUB.3 .Film Thickness on Electrochromic Performance

(101) The electrochromic performance of a-WO.sub.3 at different thicknesses was evaluated to determine how performance is affected by film thickness by successively adding up to 10 layers of films (Table 3). The ΔT values at 700 nm increases from 29% to 70% from 1-5 layers, respectively. Although additional layers led to darker coloration, they did not benefit the optical modulation, which was reduced to 62% with 10 layers, because of the compromised transparency of the thicker layers. Moreover, switching times and CE values were both found to be inversely proportional to film thickness. The coloring and bleaching times of 2 s observed for one layer increased to >20 s for 10 layers, while a coloration efficiency of 193 cm.sup.2/C decreased to 117 cm.sup.2/C with 10 layers.

(102) TABLE-US-00003 TABLE 3 Performance parameters as a function of active layer thickness for devices assembled with photo-deposited WO.sub.3 annealed at 100° C. for 1 hr..sup.a ΔT t.sub.c,90% t.sub.b,90% CE # layers.sup.b (%) (s) (s) (cm.sup.2/C) 1 29 2 2 193 3 55 9 3 153 5 70 12 5 133 7 68 28 13 118 10 62 24 23 117 .sup.aColored and bleached states produced at −3.5 and +3.0 V, respectively. Optical data measured at 700 nm. Values for ΔT, t.sub.c,90%, t.sub.b,90% and CE are also shown in FIG. 25. .sup.bSEM cross-sectional imaging verified film thicknesses of 200 and 600 nm for 1 and 5 layers, respectively.

Example 8: WO.SUB.3 .NIRDD

(103) In this example, the transparent conductive oxide is prepared in the same manner as Example 1. Anhydrous ethanol is added to tungsten (VI) chloride (WCl.sub.6, Sigma-Aldrich) to make a 0.25 M solution. This solution is stirred for 16 hours and spin-coated onto a substrate (3000 rpm, 60 s) yielding a dark blue film on the substrate. The substrate is then placed under an IR lamp for decomposition of the precursor to form a-WO.sub.3, and transformation to the metal oxide is monitored by X-ray fluorescence. The amorphous or crystalline phase can be obtained through annealing after the conversion to the oxide. The electrochromic devices were assembled as described in Example 3.

Example 9: LiNiO.SUB.x .and Other Mixed Metal Compositions by UV Photodecomposition or NIRDD

(104) In this example, the transparent conductive oxide was prepared in the same manner as Example 1. A 0.2 M solution of nickel (II) 2-ethylhexanoate (78% (w/w) in 2-ethylhexanoic acid, Strem Chemicals) and lithium 2-ethylhexanoate (Strem Chemicals) was prepared in hexanes with varying ratios of Li:Ni, for example 25:75, 40:60, 50:50, 75:25. The solution is applied to the TCO substrate and spin-coated onto a substrate (3000 rpm, 60 s). The precursors are decomposed under either a UV lamp (I=185 or I=185, 254 nm) or an IR lamp to form a-LiNiO.sub.x.

(105) Transformation to the metal oxide was monitored as in Example 1. The electrochromic devices were assembled as described in Example 3.

Example 10: V.SUB.2.O.SUB.5 .UV Photodecomposition

(106) In this example, the transparent conductive oxide was prepared in the same manner as Example 1. Anhydrous ethanol was added to vanadium (**111**) chloride (VCl.sub.3, Sigma-Aldrich) to make a 0.25 M solution. This solution was stirred for 16 hours and spin-coated onto a substrate (3000 rpm, 60 s) yielding a dark blue film on the substrate. The substrate was then placed under a UV lamp (I=185 or I=185, 254 nm) for decomposition of the precursor to form a-V.sub.2O.sub.5. Transformation to the metal oxide was monitored as in Example 4.

(107) FIG. **13***a* depicts a plot of the chlorine content for vanadium chloride precursor film on FTO

glass as a function of irradiation time, as measured by XRF analysis, and confirmed complete decomposition of the precursor after 10 min of irradiation. FIGS. **13***b* and **13***c* show that the XPS analysis of the metal oxide films on FTO glass is consistent with the formulation of as-prepared V.sub.2O.sub.5 on FTO glass. FIG. **13***c* is an expanded XPS spectrum featuring V2p.sub.1/2 and V2p.sub.3/2 signals at 525.40 eV and 517.85 eV, respectively, that are diagnostic of V.sup.5+. FIG. **13***d* is an IR spectra of an ethanolic solution of VCl.sub.5 spin-cast on FTO glass before (fresh) and after (photolyzed) being subjected to UV irradiation for 10 min. The as-prepared oxide film annealed at 100° C. for 1 hr is also indicated (annealed) in FIG. **13***d*.

Example 11: V.SUB.2.O.SUB.5 .NIRDD

(108) In this example, the transparent conductive oxide is prepared in the same manner as Example 1. Anhydrous ethanol is added to vanadium (III) chloride (VCl.sub.3, Sigma-Aldrich) to make a 0.25 M solution. This solution is stirred for 16 hours and spin-coated onto a substrate (3000 rpm, 60 s) yielding a dark blue film on the substrate. The substrate is then placed under an IR lamp for decomposition of the precursor to form a-V.sub.2O.sub.5, and transformation to the metal oxide is monitored by X-ray fluorescence. The amorphous or crystalline phase can be obtained through annealing after the conversion to the oxide. The electrochromic devices were assembled as described in Example 3.

Example 12: Nb.SUB.2.O.SUB.5 .UV Photodecomposition

(109) In this example, the transparent conductive oxide was prepared in the same manner as Example 1. Anhydrous ethanol was added to niobium (V) chloride (NbCl.sub.5, Sigma-Aldrich) to make a 0.25 M solution. This solution was stirred for 16 hours and spin-coated onto a substrate (3000 rpm, 60 s) yielding a dark blue film on the substrate. The substrate was then placed under either a UV lamp (I=185 or I=185, 254 nm) for decomposition of the precursor to form a-Nb.sub.2O.sub.3. Transformation to the metal oxide was monitored as in Example 4. The electrochromic devices were assembled as described in Example 3.

(110) FIG. **15***a* depicts a plot of the chlorine content for niobium chloride precursor film on FTO glass as a function of irradiation time, as measured by XRF analysis, and confirmed complete decomposition of the precursor after 10 min of irradiation. FIGS. **15***b* and **15***c* show that the XPS analysis of the metal oxide films on FTO glass is consistent with the formulation of as-prepared Nb.sub.2O.sub.5 on FTO glass. FIG. **15***c* is an expanded XPS spectrum featuring Nb3d.sub.3/2 and Nb3d.sub.5/2 signals at 210.10 eV and 207.40 eV, respectively, that are diagnostic of Nb.sup.5+. FIG. **15***d* is an IR spectra of an ethanolic solution of NbCl.sub.5 spin-cast on FTO glass before (fresh) and after (photolyzed) being subjected to UV irradiation for 10 min. The as-prepared oxide film annealed at 100° C. for 1 h is also indicated (annealed) in FIG. **15***d*.

Example 13: Nb.SUB.2.O.SUB.5 .NIRDD

(111) In this example, the transparent conductive oxide is prepared in the same manner as Example 1. Anhydrous ethanol is added to niobium (V) chloride (NbCl.sub.5, Sigma-Aldrich) to make a 0.25 M solution. This solution is stirred for 16 hours and spin-coated onto a substrate (3000 rpm, 60 s) yielding a dark blue film on the substrate. The substrate is then placed under an IR lamp for decomposition of the precursor to form a-Nb.sub.2O.sub.3, and transformation to the metal oxide is monitored by X-ray fluorescence. The amorphous or crystalline phase can be obtained through annealing after the conversion to the oxide. The electrochromic devices were assembled as described in Example 3.

Example 14: MoO.SUB.3 .UV Photodecomposition

(112) In this example, the transparent conductive oxide was prepared in the same manner as Example 1. Anhydrous ethanol was added to molybdenum (V) chloride (MoCl.sub.5, Sigma-Aldrich) to make a 0.25 M solution. This solution was stirred for 16 hours and spin-coated onto a substrate (3000 rpm, 60 s) yielding a dark blue film on the substrate. The substrate was then placed under either a UV lamp (I=185 or I=185, 254 nm) or an IR lamp for decomposition of the precursor to form a-MoO.sub.3. Transformation to the metal oxide was monitored as in Example 4. The

electrochromic devices were assembled as described in Example 3.

(113) FIG. **17***a* depicts a plot of the chlorine content for molybdenum chloride precursor film on FTO glass as a function of irradiation time, as measured by XRF analysis, and confirmed complete decomposition of the precursor after 30 min of irradiation. FIGS. **17***b* and **17***c* show that the XPS analysis of the metal oxide films on FTO glass is consistent with the formulation of as-prepared MoO_3 on FTO glass. FIG. **17***c* is an expanded XPS spectrum featuring $Mo3d_{3/2}$ and $Mo3d_{5/2}$ signals at 236.28 eV and 233.15 eV, respectively, that are diagnostic of Mo^{6+}. FIG. **17***d* is an IR spectra of an ethanolic solution of $MoCl_5$ spin-cast on FTO glass before (fresh) and after (photolyzed) being subjected to UV irradiation for 30 min. The as-prepared oxide film annealed at 100° C. for 1 h is also indicated (annealed) in FIG. **17***d*.

Example 15: MoO_3 .NIRDD

(114) In this example, the transparent conductive oxide is prepared in the same manner as Example 1. Anhydrous ethanol is added to molybdenum (V) chloride ($MoCl_5$, Sigma-Aldrich) to make a 0.25 M solution. This solution is stirred for 16 hours and spin-coated onto a substrate (3000 rpm, 60 s) yielding a dark blue film on the substrate. The substrate is then placed under an IR lamp for decomposition of the precursor to form a-MoO_3, and transformation to the metal oxide is monitored by X-ray fluorescence. The amorphous or crystalline phase can be obtained through annealing after the conversion to the oxide. The electrochromic devices were assembled as described in Example 3.

Example 16: Use of Amorphous TiO_2 .as an Ion Storage Material in an EC Device

(115) Amorphous TiO_2 films were produced using the solution-based photodeposition methods of the present invention. To form the TiO_2 film, 155 mg Ti(IV) 2-ethylhexanoate were dissolved in 1 mL HPLC-grade isopropanol yielding a 0.25 M solution. This solution was pipetted onto a FTO-coated glass substrate and spun cast at 3000 rotations per minute for 1 minute (Laurell model WS-650MZ-23NPP-Lite). The resultant precursor films were subjected to 10 minutes of UV (Atlantic Ultraviolet G18T5VH/U; Imax=185) irradiation. The films were annealed in an oven (Ney Vulcan 3-550) in air at different temperatures for 1 h with a ramping rate of 10° C./min. The WO_3 films were produced by the same procedures except that 0.22 M WCl_6 isopropanol solution were used as the precursor solution and UV irradiation time was 5 min.

(116) The resulting amorphous TiO_2 film can be crystallized to anatase TiO_2 (JCPDS 021-1272) at 400° C. The crystalline TiO_2 film displays an almost identical morphology to amorphous films, with a thickness of about 60 nm, slightly thinner than amorphous films.

(117) FIG. **24***a* is a schematic depiction of an EC device employing TiO_2 as an ion storage material and WO_3 as the electrochromic layer. The EC device was assembled using the same method described in Example 3.

(118) FIG. **24***b* depicts the maximum and minimum transmittance at wavelength of 700 nm over 1000 cycles for EC devices with WO_3 as the electrochromic layer, a-TiO_2 (light grey) and crystalline c-TiO_2 (dark grey) deposited on FTO as the counter electrode, to be further compared to bare FTO (black). For each cycle, the device was coloured at −3.5 V for 30 s and subsequently bleached at +3.0 V for another 30 s. As shown in FIG. **24***b*, the EC device with a TiO_2 coating as the counter electrode showed enhanced cycling stability compared to a device using bare FTO. This may be due a protective effect provided by the thin layer of TiO_2 film on FTO, which protect the crystalline FTO substrate from degradation, as shown by the retention of low internal resistance of the device using a-TiO_2 at the counter electrode after cycling 1000 times (Table 4).

(119) TABLE-US-00004 TABLE 4 Internal resistance[a] across the electrodes of the EC device before and after cycling for devices with FTO and a-TiO_2 on FTO as the counter electrode Counter Resistance before Resistance after electrode cycling (Ω) 1000 cycles (Ω) FTO 35 378 a-TiO_2 on FTO 32 33 [a]The resistance was measured by iR compensation

Example 17: Preparation of a Solid State Electrochromic Device

(120) The WO.sub.3 and NiO.sub.x films were synthesized by slight modification of the previously reported method.
(121) To prepare the WO.sub.3 film for use in the solid state EC device, a precursor solution prepared by dissolving 0.4 g WCl.sub.6 in 4 ml 2-propanol (0.25 M) was spin-coated on FTO glass at 3000 rpm for 60 s (Laurell model WS-650MZ-23NPP-Lite). The resultant precursor thin films were subjected to UV (Atlantic Ultraviolet G18T5VH/U; λ.sub.max=185) irradiation until complete decomposition was confirmed by monitoring the chlorine content using XRF analysis.
(122) To prepare the NiO.sub.x film for use as an ion storage material in the solid state EC device, a NiCl.sub.2 aqueous solution (0.25 M) was used as precursor solution and the remaining procedures remain the same as for the preparation of the WO.sub.3 film. FIG. **21***a* is a schematic illustration showing UV light irradiation of spin-casted NiCl.sub.2 precursor films on FTO glass lead to formation of amorphous NiO.sub.x (a-NiO.sub.x).
(123) Analysis of the resulting a-NiO.sub.x film is depicted in FIGS. **21***b* to **21***d*. FIG. **21***b* depicts a plot of the chlorine of CI in precursor film determined by XRF analyzer as a function of UV irradiation time, and confirm that chloride ions are completely removed by UV light in 8 hours. FIG. **21***c* is an XPS spectra of NiCl.sub.2 precursor and as-formed NiO.sub.x in binding energy range corresponding to Cl 2p. No Cl 2p signal appears in as-formed NiO.sub.x, confirming fully decomposition of chloride ions in by UV irradiation. FIG. **21***d* is an XPS spectrum of NiO.sub.x in the binding energy range corresponding to Ni 2p, matching well with that of Ni.sup.2+.
(124) To prepare the electrolyte for use in the solid state device, LiClO.sub.4 and PMMA were dried in an oven at 100° C. for overnight. Propylene carbonate (PC) was dried overnight by adding Molecular Sieve Type-3A with a w/v of 20%. The molecular sieves were activated before use by annealing at 300° C. for overnight. 0.532 g LiClO.sub.4 was dissolved in 10 ml propylene carbonate to form a 0.5 M solution. 1.339 g PMMA was then added to the LiClO.sub.4—PC solution under magnetic stirring. The mixtures were stirred and heated at 60° C. on a hot plate for overnight to form a transparent colorless gel electrolyte.
(125) Prior to assembly of the device, prelithiation of NiO.sub.x films was carried out in a 1 M-LiClO.sub.4 propylene carbonate electrolyte using a conventional three electrode system with NiO.sub.x films on FTO glass as working electrode, Ag/AgCl as reference electrode, and Pt wire as counter electrode. The lithium ions were injected into NiO.sub.x by applying a potential of −1.5 V (vs Ag/AgCl) for 10 min. Electrochromic devices were fabricated by placing a 2×2 cm square silicone rubber sheet (50 A, thickness=1 mm; McMaster-CARR) with a centered hollow circle (diameter=1.6 cm) on top of prelithiated NiO.sub.x film on FTO glass that serves as the counter electrode. A gel electrolyte of LiClO4-PC-PMMA was then drop-casted into the hollow circle. FTO glass was then coated with the WO.sub.3 films (working electrode) laid on top the silicon spacer to form a closed cell. Epoxy glue was used to seal the cell. The assembled device had an active area of 2.0 cm.sup.2. The assembled devices were heated at 60° C. in an oven for overnight before property characterization.
(126) FIG. **22***a* is a schematic depiction of the architecture of a solid state EC device using an NiO.sub.x film on the FTO glass counter electrode as an ion storage material.
(127) FIG. **22***b* shows a comparison of the transmittance spectra obtained for EC devices prepared with and without a-NiO.sub.x on the FTO glass counter electrode at bleached and colored state. The spectra were recorded after coloring at −2.1 V or bleaching at +2.1 V for 60 s.
(128) FIG. **22***c* shows the transmittance change at wavelength of 633 nm for the EC device prepared with a-NiO.sub.x on FTO as counter electrode as a function of time. The device was bleached at +2.1 V for 30 s, then colored at −2.4 V for another 30 s. Switch times are indicated.
(129) FIG. **22***d* shows changes in optical density at 633 nm as a function of charge density for a solid state EC device prepared using a-NiO.sub.x on the FTO glass counter electrode.
Example 18: Comparison of Solid State EC Devices Prepared Using Amorphous and Crystalline NiO as Counter Electrodes

(130) FIG. **23***a* shows a comparison of transmittance spectra of EC devices prepared using a-NiO.sub.x and c-NiO films prepared using the present methods as counter electrodes at colored and bleached state. The spectra were recorded after coloring at −2.1 V and bleaching at +2.1 V for 60 s. FIG. **23***b* depicts the transmittance change at wavelength of 633 nm for the EC devices with a-NiO.sub.x and c-NiO on FTO as counter electrode as a function of time. The devices were bleached at +2.1 V for 30 s, then colored at −2.1 V for another 30 s. Switch times are indicated. FIG. **23***c* depicts the changes in optical density of the respective devices at 633 nm as a function of charge density using a-NiO.sub.x and c-NiO on FTO as counter electrode. Coloration efficiency values were determined by fitting the linear region of the plot.
Example 19: Comparison of Solid State Devices of the Present Invention with Prior Art Devices
(131) All devices listed in Table 5 use WO.sub.3 films as electrochromic layers, NiO films as ion storage layer, and polymer-based electrolyte. The present work clearly demonstrates that the amorphous NiO films formed in accordance with the present invention show superior performance to its crystalline counterpart, which has never been previously documented. The methods of the present invention also represent a significant advancement towards using solution-processing methods for deposition of metal oxide films for use in solid state electrochromic windows.
(132) TABLE-US-00005 TABLE 5 Performance parameters of our solid state electrochromic devices in comparison to that of solid-state devices reported in the literatures Counter electrode Deposition ΔT.sup.a t.sub.c,90%.sup.b t.sub.b,90%.sup.c CE.sup.d material Phase method (%) (s) (s) (cm.sup.2/C) Reference NiO porous film crystalline chemical bath 55% 10 20 87.2 Zhang et deposition al..sup.e NiO nanoparticle crystalline inkjet printing 75% 10 13 131.9 Cai et al..sup.f film NiO.sub.x film crystalline magnetron 52% 5 2 — Liu et al..sup.g sputtering NiO film amorphous UV 60% 4 6 141.1 this work.sup.h NiO film crystalline UV 26% 78 17 72.0 this work.sup.h .sup.aMaximum optical modulation (ΔT) determined by the light transmittance difference between fully colored and bleached states at a specific wavelength .sup.bSwitching time of coloring (t.sub.c,90%) defined by the time required to reach 90% of a full transmittance change from the bleached to colored state. .sup.cSwitching time of bleaching (t.sub.b,90%) from the colored to bleached state. .sup.dColoration efficiency (CE) defined as the change in optical density acquired by injection of charge per unit area .sup.eMeasured in a potential range from −2.5 V to +2.5 V, at wavelength of 633 nm .sup.fMeasured in a potential range from −2.5 V to +2.5 V, at wavelength of 550 nm .sup.hMeasured in a potential range from −1.8 V to +1.8 V, at wavelength of 550 nm .sup.hMeasured in a potential range from −2.1 V to +2.1 V, at wavelength of 633 nm
Example 20: Photodeposition of Electrochromic Films on Tin-Doped Indium Oxide (ITO) Coated Polyethylene Terephthalate (PET)
(133) The methods of the present invention have also been demonstrated as useful for deposition of metal oxide films on flexible substrates.
(134) A precursor solution was prepared by rotary evaporating 4 ml of tungsten(VI) isopropoxide 5% w/v in isopropanol to approximately 2 ml. Then, 0.152 ml acetylacetone was added to the tungsten(VI) isopropoxide solution. After 30 min, the precursor solutions were spin-coated onto ITO-PET substrates at 3000 rpm for 60 s (Laurell model WS-650MZ-23NPP-Lite). The resultant precursor thin films were subjected to UV (Atlantic Ultraviolet G18T5VH/U; λ.sub.max=185) irradiation until complete decomposition of organic ligands confirmed by FTIR analyses. To produce multi-layer thin films, the spin-coating and UV light irradiation steps were repeated multiple times. The as-deposited films were annealed in an oven (Ney Vulcan 3-550) in air at 100° C. for 1 hour.
(135) The electrochromic properties were measured in a spectroelectrochemical cell that has a three electrodes configuration. WO.sub.3 film on ITO-PET was used as working electrode, Ag/AgCl as reference electrode, and Pt as counter electrode. 1 M-LiClO.sub.4 propylene carbonate was used as electrolyte. The optical properties were recorded by PerkinElmer Lambda 35 UV-Vis spectrophotometer. The potentials were applied by a CHI660D potentiostat.

(136) FIG. **26***a* shows the transmittance spectra of coloured and bleached WO.sub.3 on ITO-coated PET plastic substrate after holding the potential at −/+0.7 V (vs Ag/AgCl) for 60 seconds. The photographs are the photodeposited WO.sub.3 film on ITO-PET substrate at bleached and colored states.
(137) FIG. **26***b* shows the transmittance change at 700 nm as a function of time. The WO.sub.3 film was held at potential of +0.7 V for 30 s and followed by another 30 seconds at −0.7 V. Switching times are indicated.
Example 21: Effect of Nb Doping on WO.SUB.3 .Film Performance
(138) For the synthesis of WO.sub.3 film, a 0.25 M WCl.sub.6 isopropanol precursor solution was prepared by dissolving 0.200 g WCl.sub.6 in 2 ml of 2-propanol. The precursor solution for the 10% Nb-doped WO.sub.3 was prepared by adding 0.43 ml of the 0.1 M NbCl.sub.5 ethanol solution into 1.57 ml of 0.25 M WCl.sub.6 isopropanol solution. The precursor solutions were then spin-coated on FTO glass at 3000 rpm for 60 s (Laurell model WS-650MZ-23NPP-Lite). The resultant precursor thin films were subjected to UV (Atlantic Ultraviolet G18T5VH/U; λ.sub.max=185) irradiation for 15 min. To produce multi-layer thin films, the spin-coating and UV light irradiation steps were repeated multiple times. The as-deposited films were annealed in an oven (Ney Vulcan 3-550) in air at 100° C. for 1 hour.
(139) The electrochromic properties were measured in a spectroelectrochemical cell that has a three electrodes configuration. Doped or undoped WO.sub.3 film on FTO glass was used as working electrode, Ag/AgCl as reference electrode, and Pt as counter electrode. 1 M-LiClO.sub.4 propylene carbonate was used as electrolyte. The optical properties were recorded by PerkinElmer Lambda 35 UV-Vis spectrophotometer. The potentials were applied by a CHI660D potentiostat.
(140) FIG. **26***a* shows a comparison of the transmittance spectra for undoped WO.sub.3 (black) and Nb-doped WO.sub.3 (grey) on FTO glass after holding the potential at −0.8 V (coloring) and −0.8 V (bleaching) (vs Ag/AgCl) for 60 seconds. FIG. **26***b* shows a comparison of the tansmittance change as a function of time over 10 electrochromic cycles for undoped WO.sub.3 (black) and Nb-doped WO.sub.3 (grey). In each cycle the films were held at −0.8 V (vs Ag/AgCl) for 30 seconds followed by another 30 seconds at +0.8 V.
Example 22: Effect of Ti Doping on WO.SUB.3 .Film Performance
(141) A 0.25 M WCl.sub.6 isopropanol precursor solution was prepared by dissolving 0.200 g WCl.sub.6 in 2 ml 2-propanol. A 0.25 M Ti(IV) 2-ethylhexanoate precursor solution was prepared by dissolving 0.282 g Ti (IV) 2-ethylhexanoate in 2 ml 2-propanol. The precursor solutions for the 1%, 5%, 10% Ti-doped WO.sub.3 were prepared by mixing 0.02 ml, 0.10 ml, and 0.20 ml 0.25 M Ti(IV) 2-ethylhexanoate isopropanol solutions with 1.98 ml, 1.9 ml, and 1.8 ml 0.25 M WCl.sub.6 isopropanol solutions respectively. The precursor solutions were then spin-coated on FTO glass at 3000 rpm for 60 s (Laurell model WS-650MZ-23NPP-Lite). The resultant precursor thin films were subjected to UV (Atlantic Ultraviolet G18T5VH/U; λ.sub.max=185) irradiation for 10 min. To produce multi-layer thin films, the spin-coating and UV light irradiation steps were repeated multiple times. The as-deposited films were annealed in an oven (Ney Vulcan 3-550) in air at 100° C. for 1 hour.
(142) The electrochromic properties were measured in a spectroelectrochemical cell that has a three electrodes configuration. Doped or undoped WO.sub.3 film on FTO glass was used as working electrode, Ag/AgCl as reference electrode, and Pt as counter electrode. 1 M-LiClO.sub.4 propylene carbonate was used as electrolyte. The optical properties were recorded by PerkinElmer Lambda 35 UV-Vis spectrophotometer. The potentials were applied by a CHI660D potentiostat.
(143) FIG. **27** depicts the maximum and minimum transmittance over 1000 cycles for undoped and Ti-doped WO.sub.3 films. In each cycle the films were held at −0.8 V (vs Ag/AgCl) for 30 seconds followed by another 30 seconds at +0.8 V.
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Claims

1. A process for forming an electrochromic material suitable for use in an electrochromic device, the process comprising: providing a transparent conductive substrate; coating the transparent conductive substrate with a solution of one or more metal precursors, wherein a metal precursor comprises a ligand selected from chloride, bromide and nitrate and is converted to a metal oxide upon exposure to UV radiation and/or ozone; and exposing the coated transparent conductive substrate to UV radiation and/or ozone in an aerobic atmosphere at ambient temperature and ambient pressure to effect conversion of the one or more metal precursors to a metal oxide film on the transparent conductive substrate without application of a heat treatment with an external heat source, thereby forming the electrochromic material, wherein the electrochromic device comprises: a first electrode comprising the electrochromic material, a counter electrode, and an ion-conductor layer for conducting ions between the first electrode and the counter electrode.
2. The process according to claim 1, further comprising annealing the metal oxide film, wherein annealing is carried out at a temperature of about 50° C. to about 750° C.
3. The process according to claim 1, further comprising annealing the metal oxide film, wherein the annealing is carried out at about 100° C., 200° C. or 600° C. for 1 hour.
4. The process according to claim 1, wherein the metal oxide film comprises a metal oxide selected from the group consisting of NiO.sub.x, WO.sub.x, NbO.sub.x, MoO.sub.x, MnO.sub.x, CoO.sub.x, VO.sub.x, TaO.sub.x, TiO.sub.x, FeO.sub.x, IrO.sub.x, and combinations thereof, a mixed metal oxide selected from LiNiO.sub.x, TiWO.sub.x, and FeNiO.sub.x, or a doped metal oxide selected from Nb doped WO.sub.3 and Ti doped WO.sub.3.
5. The process according to claim 4, wherein the metal oxide film comprises WO3.
6. The process according to claim 1, wherein the transparent conductive substrate is formed of a conductive material.
7. The process according to claim 1, wherein the transparent conductive substrate is formed of a transparent material coated with a conductive film.
8. The process according to claim 7, wherein the transparent conductive substrate is a substrate coated with fluorine tin oxide (FTO), indium tin oxide (ITO), or aluminum zinc oxide (AZO).
9. The process according to claim 1, wherein coating and exposing are repeated until a desired thickness of the metal oxide film is achieved.
10. The process according to claim 1, wherein the metal oxide film is an amorphous metal oxide film.
11. The process according to claim 1, wherein the metal oxide film is a crystalline metal oxide film.
12. The process according to claim 1, wherein the first electrode comprises FTO glass coated with an amorphous WO.sub.3 film.
13. The process according to claim 1, wherein the counter electrode comprises bare FTO glass.
14. The process according to claim 1, wherein the metal oxide film is a first metal oxide film and the counter electrode comprises FTO glass coated with a second metal oxide film prepared using the process as defined in claim 1.
15. The process according to claim 14, wherein the counter electrode comprises FTO glass coated with NiO.sub.x or TiO.sub.x.
16. The process according to claim 1, wherein the ion-conductor layer is an electrolytic solution.

17. The process according to claim 16, wherein the electrolytic solution is a LiClO.sub.4-propylene carbonate electrolyte solution.

18. The process according to claim 1, wherein the electrochromic device is a solid-state device and the ion-conductor layer is an electrolytic gel.

19. The process according to claim 18, wherein the ion-conductor layer is LiClO.sub.4-propylene carbonate-poly (methyl methacrylate) gel electrolyte.

20. The process according to claim 7, wherein the transparent conductive substrate is indium tin oxide (ITO) coated polyethylene terephthalate (PET).