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(54) **ELECTROCHROMIC DEVICE HAVING THREE-DIMENSIONAL ELECTRODE**

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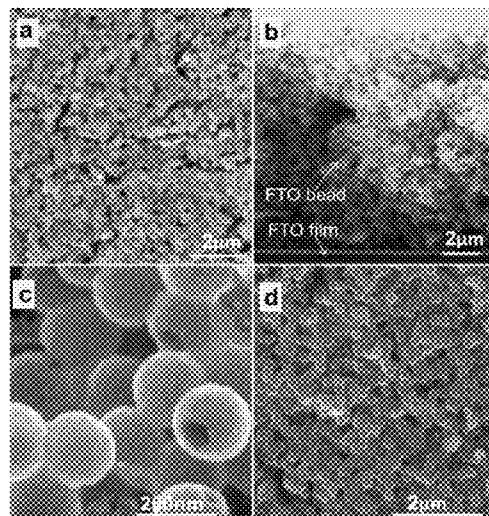
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ABSTRACT

An electrochromic device comprises (i) a conductive layer, (ii) an electrochromic material, on the conductive layer, (iii) an electrolyte, on the electrochromic material, and (iv) a counter-electrode, on the electrolyte. The conductive layer has a surface roughness factor (SRF) of at least 10, and the conductive layer comprises a semi-metal.

19 Claims, 5 Drawing Sheets



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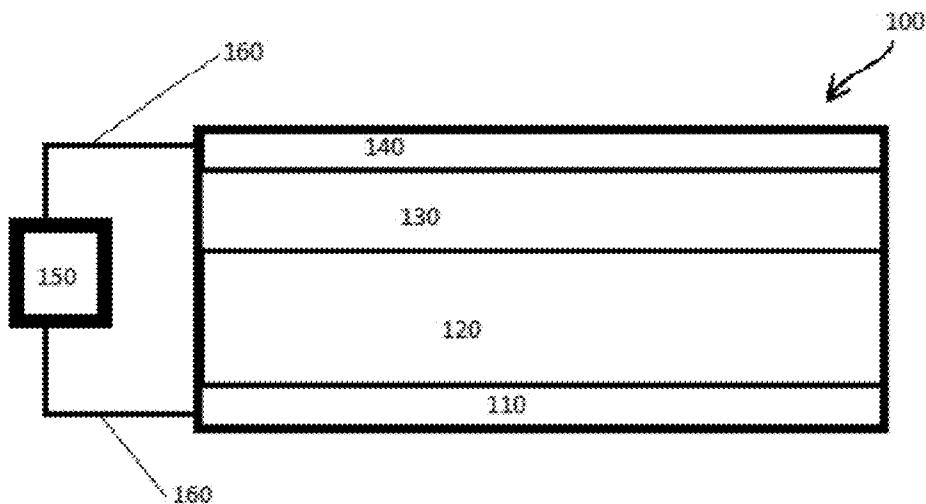


FIG. 1A

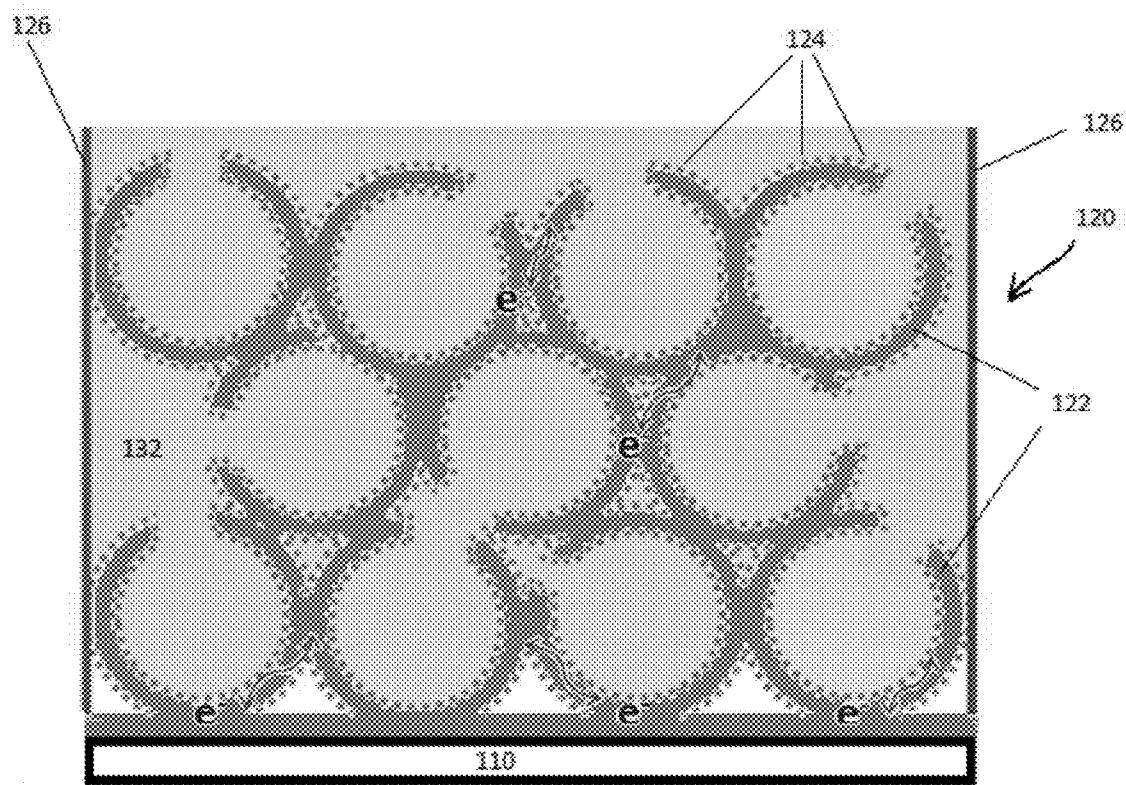


FIG. 1B

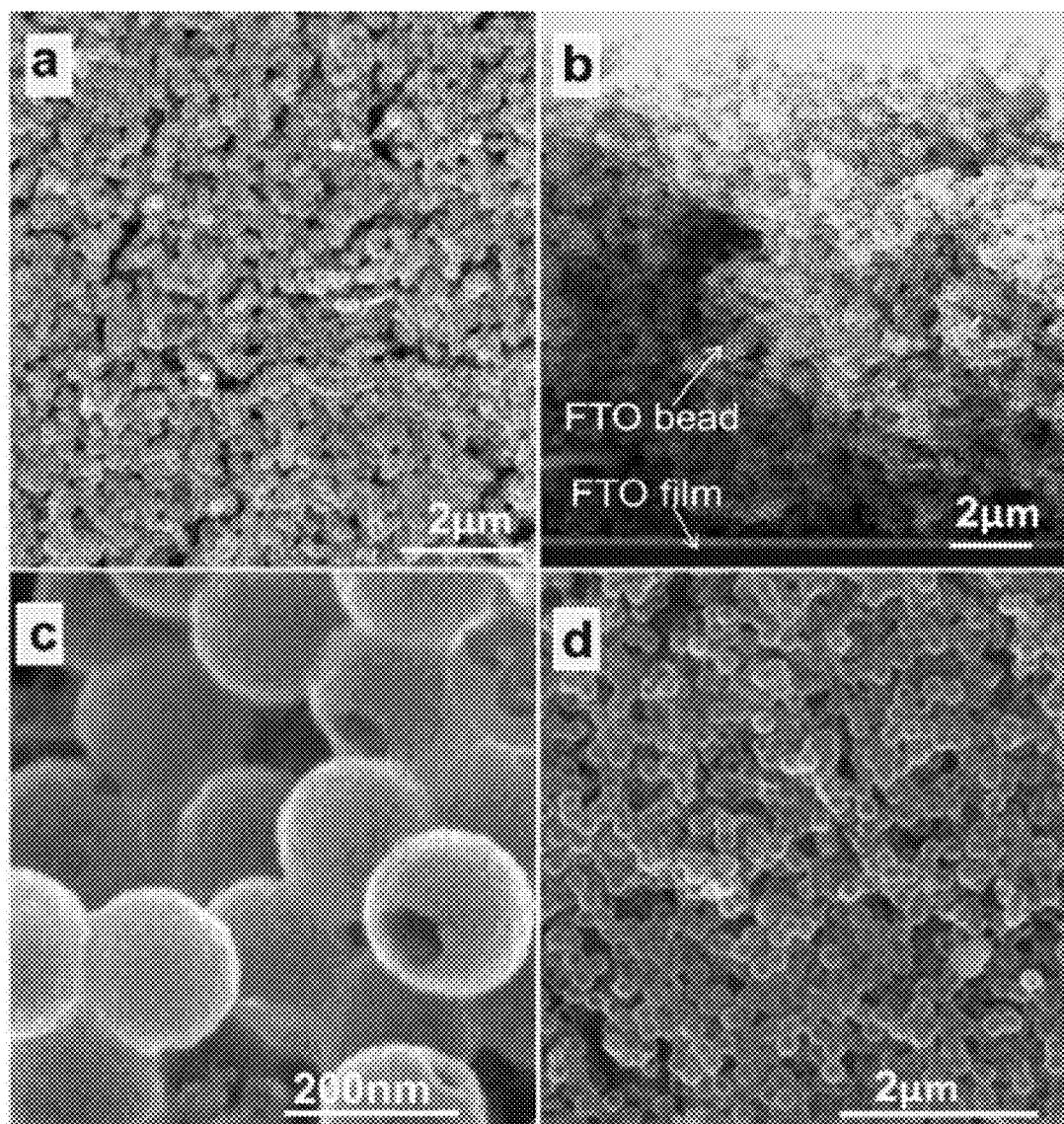


FIG. 2

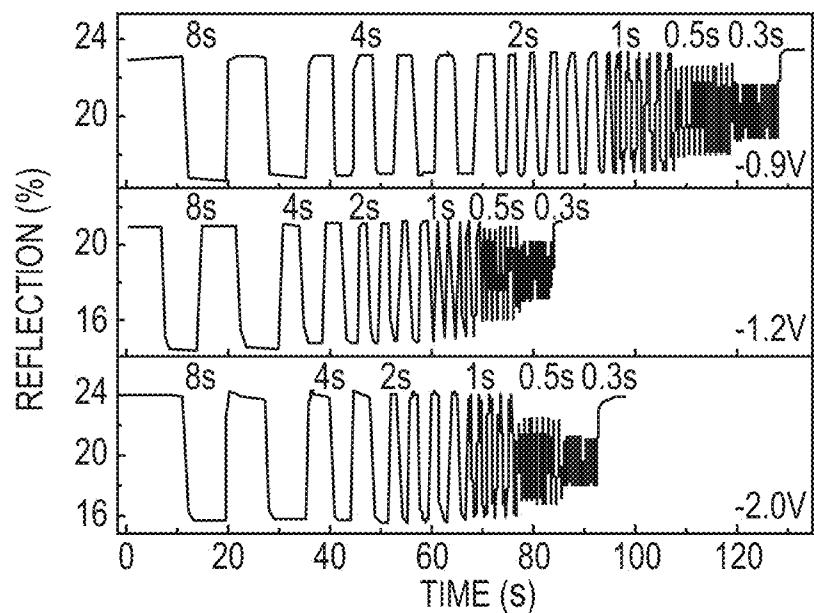


FIG. 3a

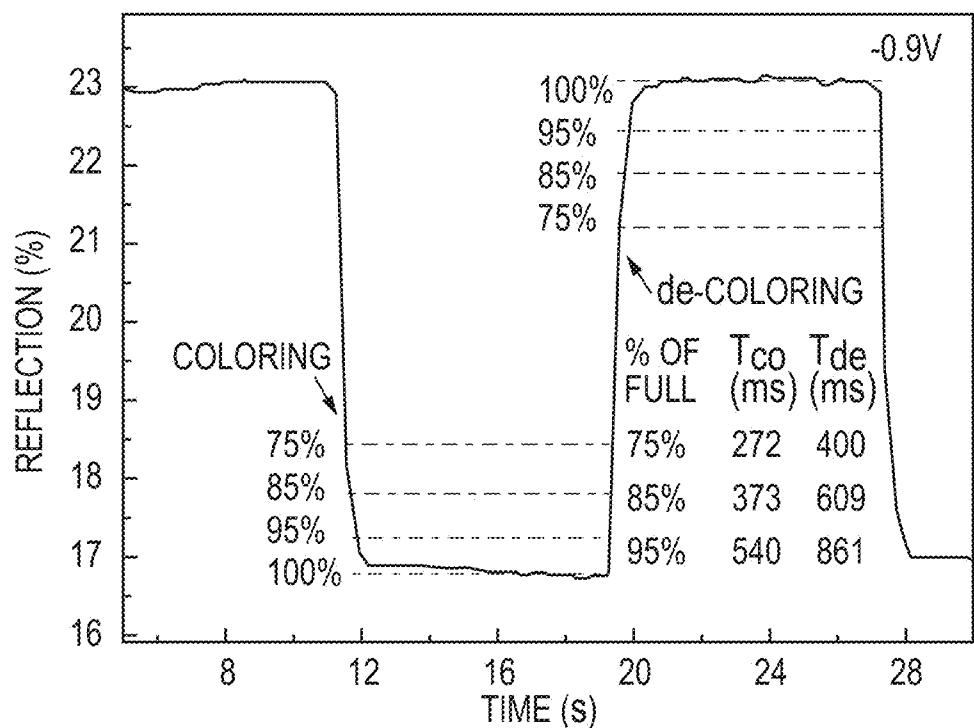


FIG. 3b

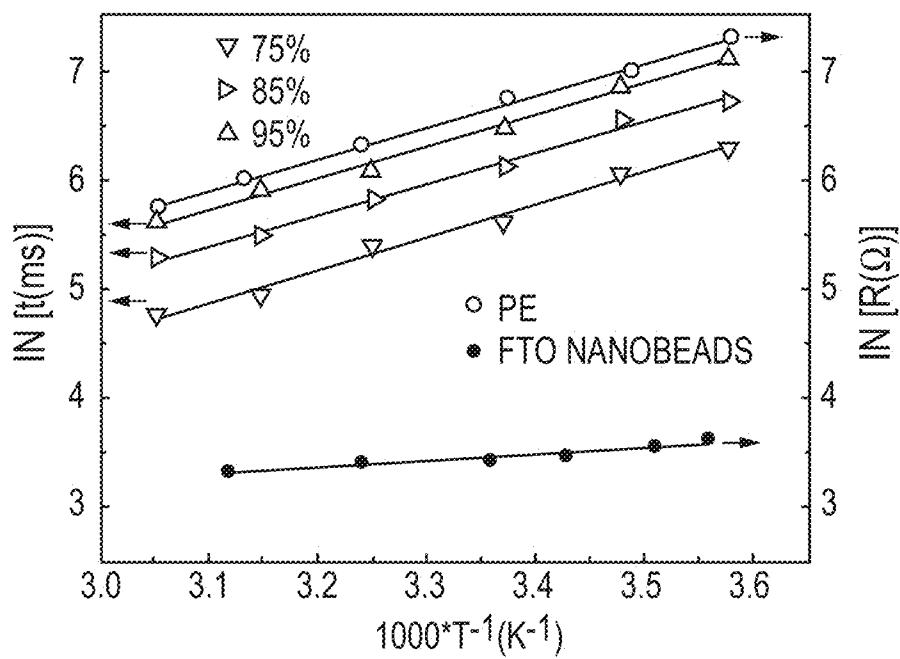


FIG. 4a

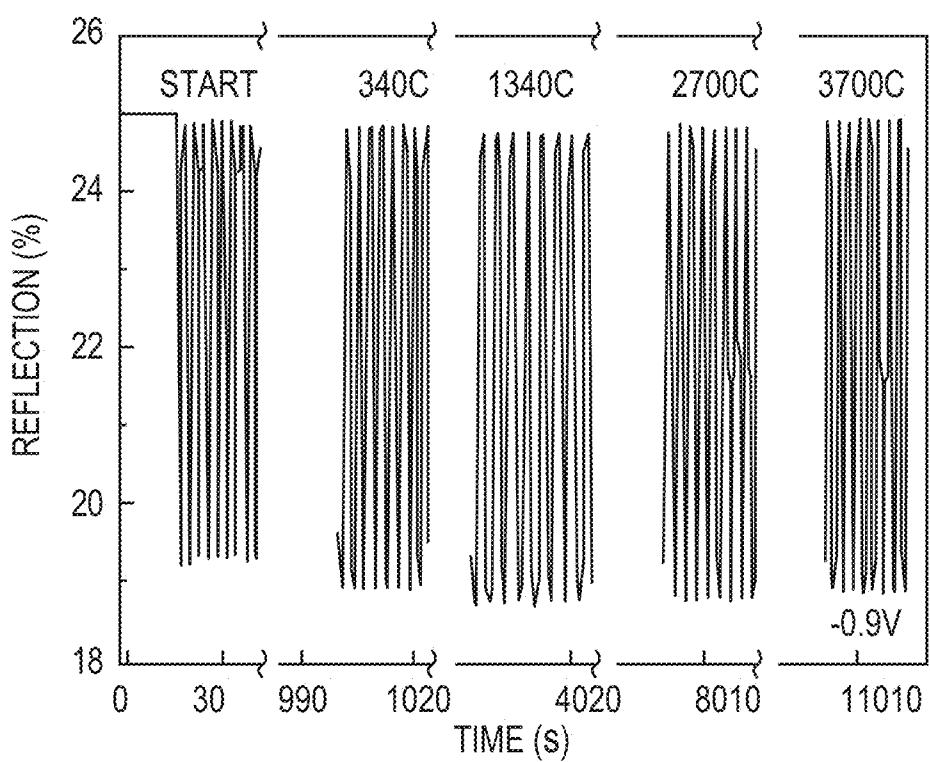


FIG. 4b

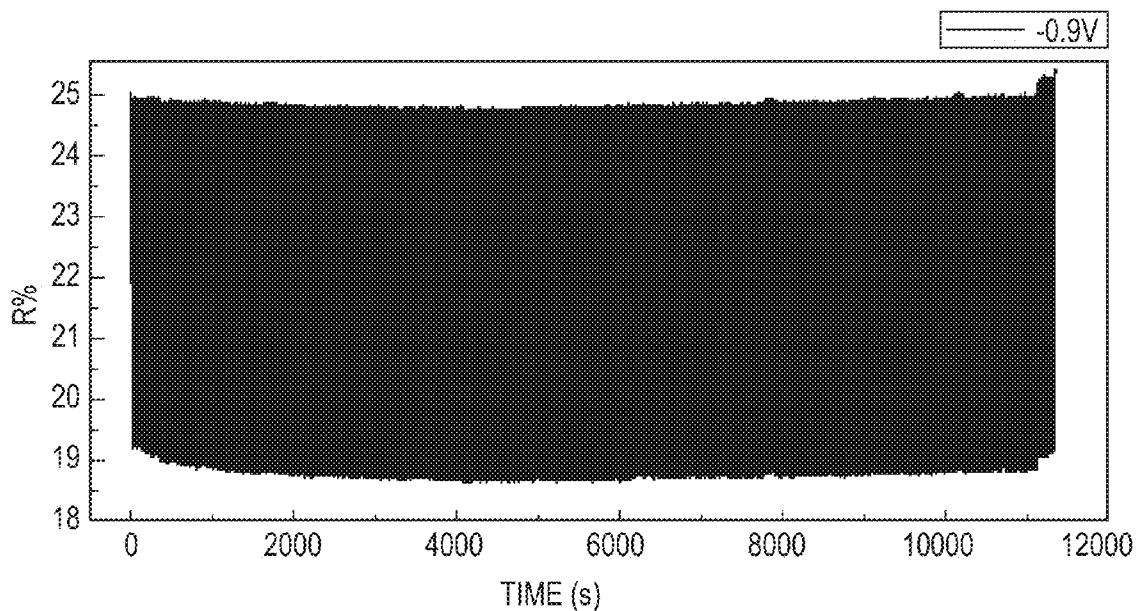


FIG. 5

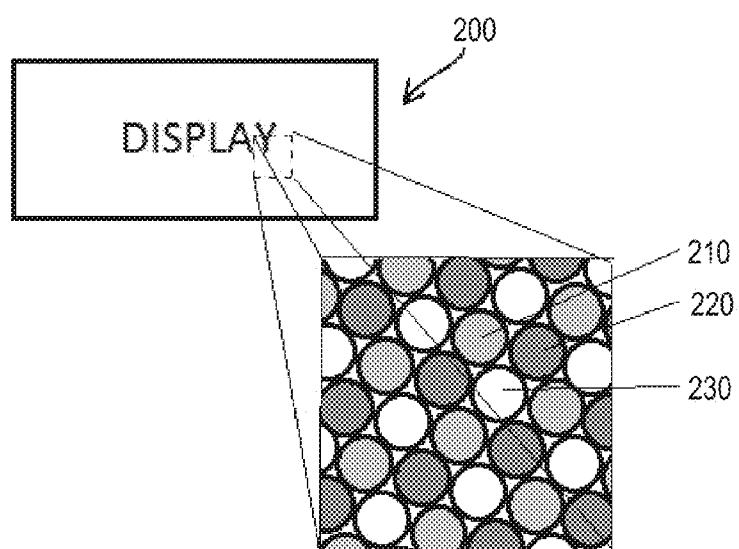


FIG. 6

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ELECTROCHROMIC DEVICE HAVING
THREE-DIMENSIONAL ELECTRODEFEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT

This invention was made with government support under CBET-1150617 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND

Electrochromic (EC) devices have been attracting widely spread attention as they can be used as smart windows and electronic displays. In particular, recent research and development progress in organic and polymer electrochromic materials exhibiting different voltage-dependent colors makes EC devices a strong candidate for sunlight-readable exterior displays. Typically, an EC device includes an electrochromic material between two electrodes and in contact with an electrolyte. A porous layer, referred to as the docking layer, is prepared from a suitable semiconductor material such as TiO_2 or ZnO , attached to one of the electrodes and separated from the other electrode by the electrolyte. The electrochromic material is absorbed or attached to the docking layer. When a high enough voltage is applied, the electrochromic material is reduced or oxidized, and changes color. For example, diethyl viologen diiodine is an electrochromic material which is colorless, and becomes darkly colored upon reduction.

However, the quest for electrochromic display technology often suffers from the dilemma of the thickness of the docking layer and the resulting slow charge diffusion that limits the switching speed of electrochromic device. Explicitly, a film with a large surface area such as a TiO_2 nanoparticulate film or a polymer film is often desired to load enough electrochromic materials for sufficient color contrast, but at a cost of high driving voltage and slow response time due to the large series resistance and slow electron mobility in the docking layer. Once an electric leak occurs between the two electrodes, the high voltage will immediately drop on the electrolyte, resulting in dielectric breakdown of the electrolytes and active electrochromic material, thus deteriorating the lifetime of the device.

SUMMARY

In a first aspect, the present invention is an electrochromic device, comprising (i) a conductive layer, (ii) an electrochromic material, on the conductive layer (iii) an electrolyte, on the electrochromic material, and (iv) a counter-electrode, on the electrolyte. The conductive layer has a surface roughness factor (SRF) of at least 10, and the conductive layer comprises a semi-metal.

In a second aspect, the present invention is an electrochromic device, comprising (i) a conductive layer, (ii) an electrochromic material, on the conductive layer (iii) an electrolyte, on the electrochromic material, and (iv) a counter-electrode, on the electrolyte. The conductive layer has a surface roughness factor (SRF) of at least 10, and the electrochromic material is not Ni oxide or hydroxide.

In a third aspect, the present invention is an electrochromic display, comprising a plurality of the electrochromic devices.

In a fourth aspect, the present invention is a process of preparing an electrochromic device, comprising forming a conductive layer, having a SRF of at least 10, applying an electrochromic material onto the conductive layer, and pre-

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paring the electrochromic device using the conductive layer and the electrochromic material. The conductive layer comprises a semi-metal.

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DEFINITIONS

Surface roughness factor (SRF) is the surface area divided by the projected substrate area. The surface area is determined by measuring the BET surface area.

10 Response time of an EC device is the greater of the coloring or de-coloring response time. The coloring response time is the time the device takes to go from a de-colored state to a colored state, using 75% of the coloring of the full colored state as an end-point. The de-coloring response time is the time the device takes to go from a colored state to a de-colored state, using 75% of the de-coloring of the fully de-colored state as an end-point. The response time is determined using the coloring voltage, where the fully colored or fully de-colored state is achieved using the coloring voltage. Preferably, the response time of the EC device is at most 1 second, more preferably at most at most 750 ms, even more preferably at most 500 ms, and most preferably at most 400 ms.

15 Coloring voltage of an EC device is the lowest voltage necessary to go from a de-colored state to 75% of the most fully colored states achievable with higher voltages. Preferably, the coloring voltage is at most 3V, more preferably at most 2V, even more preferably at most 1V, and most preferably at most 0.9V.

30 BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A and 1B show schematic diagrams of an EC device.

25 FIGS. 2a, 2b, 2c and 2d show SEM images of 3-dimensional conductive FTO hollow nanobeads: (a) Topview; (b) Cross-section; (c) Magnified image of individual FTO nanobeads; (d) FTO nanobeads coated with viologen.

30 FIGS. 3a and 3b illustrate reflection and response time of an EC device: (a) Reflection at 580 nm at different driving voltages; (b) Response time analysis of EC device.

35 FIGS. 4a and 4b illustrate response time and reversibility of an EC device: (a) Arrhenius plots: response time of coloring at different temperature at -0.9V ; (b) Reversibility test of EC device.

40 FIG. 5 is a full graph of the reversibility test at $\pm 0.9\text{V}$ of an EC device.

45 FIG. 6 is a schematic diagram of an EC display, which an enlarged portion showing the individual EC devices which make up a portion of the EC display.

50 DETAILED DESCRIPTION

The present invention makes use of the discovery that replacing the semiconductor docking layer, with a conductive layer having a surface roughness factor (SRF) of at least 10, dramatically improves the response time and reduces the driving voltage of the EC device. Preferably, the conductive layer is a semimetal, including n-type degenerate semiconductors such as fluorinated tin oxide (FTO), aluminum-zinc oxide (AZO), antimony-tin oxide (ATO) or indium-tin oxide (ITO), which are transparent. Preferably, the electrochromic material is an organic compound or polymer, rather than a metal oxide.

55 An EC device, 100, is illustrated in FIG. 1A, where components are not shown to scale. The EC device includes an optional substrate, 110, an active layer, 120, on the substrate, an electrolyte layer, 130, on the active layer, and a counter-

electrode, 140, on the electrolyte layer. Also illustrated in the figure are electrical leads, 160 and 160, which electrically connect a power source, 160, to the EC device. The power source drives and controls the color change of the EC device.

FIG. 1B, also not to scale, shows details of the active layer, 120. The active layer includes a conductive layer, 122, which has a surface roughness factor of at least 10. On the conductive layer is the electrochromic material, 124. In contact with the electrochromic material is an electrolyte, 132; the electrolyte is also present in the electrolyte layer. Also illustrated is sealing layer, 126, which may extend the full length of the EC device, and which separates, seals and/or insulates the EC device. In the illustration, arrows indicate possible electrically conductive pathways through the conductive layer.

An EC display, 200, is illustrated in FIG. 6, which is not shown to scale. The figure shows an enlarged portion of the display, which is composed of a plurality of independently addressable EC devices, which each EC device being a single pixel or section of the EC display. As shown in the figure, the EC device of the display may be different colors, preferably 3 different colors, such as a first color, 210, a second color, 220, and a third color, 230. Examples of preferred colors are red, green and blue.

Preferably, the substrate and the conductive layer are transparent, so that light may pass through the device when the electrochromic material is colorless or lightly colored, improving contrast. Alternatively, the substrate and/or the conductive layer are white, again to provide improved contrast. Examples of substrates include glass, quartz and transparent polymeric materials, such as polycarbonate. Examples of transparent conductive layers include indium-tin oxide, fluorinated tin oxide, and aluminum-zinc oxide. These transparent conductive materials are semimetals. The conductive layer may also be formed as a composite material and/or formed as multiple layers. For example, a planar substrate of glass may be coated with a layer of fluorinated tin oxide, and fine particles of fluorinated tin oxide applied to the surface and sintered together to provide the substrate and conductive layer.

A variety of techniques may be used to provide a conductive layer with a SRF of at least 10. For example, a planar substrate may be coated with a layer of conductive material, and then fine particles of the conductive material may be applied to the coated substrate and sintered together. Alternatively, a substrate may be etched to provide a substrate with a SRF of at least 10, and then coated with a conductive layer, providing a conductive layer with a SRF of at least 10. Preferably the conductive layer may have a SRF of at least 20, at least 50, at least 100, at least 400, or at least 500, including 15, 25, 30, 40, 45, 60, 70, 80, 90, 150, 200, 300, 530, 600, 700, 800, 900 and 1000.

In another alternative, a template material and a precursor of the conductive layer material may be used to form a conductive layer with an SRF of at least 10. The template may be ordered or disordered. Examples include a disordered template of polystyrene beads, which may be prepared by mixing the polystyrene beads with a precursor solution; applying a layer of the mixture to a substrate, then drying followed by sintering. An ordered template of polystyrene beads may also be used to form a conductive layer having an SRF of at least 10 (Yang et al., "Three-Dimensional Photonic Crystal Fluorinated Tin Oxide (FTO) Electrodes: Synthesis, Optic and Electrical Properties" *ACS Applied Materials & Interfaces* 2011, 3, 1101). For example, polystyrene beads having a diameter of 100 to 1000 nm, including 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900 or 950 nm, may be used. Multiple layers may also be formed,

where each layer or set of layers is formed using different sizes of polystyrene beads. Subsequent etching or an increase in the total number of layers may be used to increase the SRF of the structure.

Electrochromic materials fall into two broad classes: organic electrochromic materials, including organic molecules, organic polymers, organometallic molecules, and organometallic polymers; and inorganic electrochromic materials, including metal oxides and hydroxides. Preferably, the electrochromic material is an organic electrochromic material. Examples of organic electrochromic materials include viologens, which may be found in many different colors, including red, green and blue (G. Bar, et al. "RGB organic electrochromic cells" *Solar Energy Materials & Solar Cells* 99 (2012) 123-128; X. Tu, et al. "The synthesis and electrochemical properties of cathodic-anodic composite electrochromic materials" *Dyes and Pigments* 88 (2011) 39-43); violene/cyanine hybrids (S. Hüning, et al. "Violene/cyanine hybrids: a general structure for electrochromic systems" *Chemistry—A European Journal* Vol. 5, Issue 7 (1999) 1969-1973); metalloviologens (D. G. Kurth, et al. "A new Co(II)-metalloviologen-based electrochromic material integrated in thin multilayer films" *Chem. Commun.* (2005) 2119-2 121); organometallic complexes (F. Pichot, et al. "A Series of Multicolor Electrochromic Ruthenium(II) Trisbipyridine Complexes: Synthesis and Electrochemistry" *J. Phys. Chem. A*, 103 (31), 6263-6267 (1999)); phenothiazines (M. Grätzel "Materials science: Ultrafast colour displays" *Nature* 409 (2001) 575-576); organic polymers (B. D. Reeves, et al. "Spray Coatable Electrochromic Dioxathiophene Polymers with High Coloration Efficiencies" *Macromolecules*, 37 (20), 7559-7569 (2004); G. Sonmez, et al. "Red, Green, and Blue Colors in Polymeric Electrochromics" *Advanced Materials* 16 (21) 1905-1908 (2004)); and organometallic polymers (S. Bernhard, et al. "Iron(II) and Copper(I) Coordination Polymers: Electrochromic Materials with and without Chiroptical Properties" *Inorg. Chem.* 42 (14), 4389-4393 (2003)). Preferably, an EC display will include EC devices with at least 3 different colors, for example red, green and blue.

The electrochromic material may be applied to the conducting layer by applying a solution of the electrochromic material to the conducting layer, or by vapor phase deposition.

Although inorganic electrochromic materials are possible, they are less preferred, and preferably inorganic electrochromic materials are not used, more preferably metal oxides are not used. Examples of inorganic electrochromic materials include oxides and hydroxides Ni, W, Ti, Mo and Ir. Metal oxide electrochromic materials are less preferred, because they are usually formed by oxidizing a metal framework, requiring the conducting layer to be formed of the metal or a compound of the metal. In these cases, only a single electrochromic material will be present (the metal oxide), preventing the formation of an EC display which includes more than a single color of electrochromic material. Furthermore, the metal or compound of the metal which forms the conducting layer may not be white or transparent, reducing the contrast available with the device.

An electrolyte, present in the conducting layer and which forms the electrolyte layer, may be a liquid, polymer, or an ionic liquid. Liquid electrolytes include solutions of one or more salts dissolved in one or more polar solvents; examples of solvents include water, alcohols, N-methylformamide (NMF), propylene carbonate (PC) and dimethyl sulfoxide (DMSO); examples of salts include NH₄I, LiCl, LiClO₄, NaCl, and Na₂SO₄. Preferably, the solvent is a non-aqueous

solvent. A liquid electrolyte may be a sol-gel electrolyte, which is a liquid electrolyte containing a gelling agent; examples of gelling agents included polymers and copolymers which are soluble in the solvent of the liquid electrolyte, or which can be polymerized in situ by adding the appropriate monomer to the liquid electrolyte follow by initiation of the polymerization reaction. Examples of gelling agents include polyvinyl alcohols, copolymers of acrylates and methacrylates, polyacrylonitrile, polyethylene oxide, polyethylene glycol and polyvinylpyrrolidone (S. Seki, et al. "Effect of binder polymer structures used in composite cathodes on interfacial charge transfer processes in lithium polymer batteries" *Electrochimica Acta*, Vol. 50, Issues 2-3 (2004) 379-383). Polymer electrolytes are electrolytes where the ions of the electrolyte include a polymer (W. Li, et al. "A novel polymer quaternary ammonium iodide and application in quasi-solid-state dye-sensitized solar cells" *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 170, Issue 1 (2005), 1-6; J. Kang, et al. "Polymer electrolytes from PEO and novel quaternary ammonium iodides for dye-sensitized solar cells" *Electrochimica Acta*, Vol. 48, Issue 17 (2003) 2487-2491; G. Wang, et al. "Gel polymer electrolytes based on polyacrylonitrile and a novel quaternary ammonium salt for dye-sensitized solar cells" *Materials Research Bulletin* Vol. 39, Issue 13 (2004) 2113-2118; X.-G. Sun, et al. "Comb-shaped single ion conductors based on polyacrylate ethers and lithium alkyl sulfonate" *Electrochimica Acta*, Vol. 50, Issue 5 (2005) 1139-1147). Ionic liquids are salts which are liquid at or near room temperature, and may not require the presence of a solvent (H. Ohno, et al. "Development of new class of ion conductive polymers based on ionic liquids" *Electrochimica Acta*, Vol. 50, Issues 2-3 (2004) 255-261; M. Morita, et al. "Ionic conductance behavior of polymeric gel electrolyte containing ionic liquid mixed with magnesium salt" *Journal of Power Sources*, Vol. 139, Issues 1-2 (2005) 351-355). The electrolyte may be applied as a liquid. In the case of non-liquid electrolytes, a solution may be applied, allowing the solvent to evaporate. In the case of solid polymer electrolyte, in situ polymerization of monomers may be carried out, using a solution of the monomer or a neat mixture of the monomers.

The counter electrode is a transparent conducting material, which may optionally be present on the surface of a substrate material. Examples include indium-tin oxide, fluorinated tin oxide, antimony-tin oxide and aluminum-zinc oxide, or any of these materials on glass, quartz or transparent polymeric materials, such as polycarbonate.

The sealing layer may be any material which prevent contamination of the device from the outside environment, and which prevents liquid electrolyte from leaking out of the device. Sealing layer materials include metals, plastics, epoxy resins and polydimethylsiloxane (PDMS).

EXAMPLES

In this example is shown that a conductive 3-dimensional FTO hollow nanobead electrode can significantly enhance the response time of EC devices to less than 300 ms, a factor 10 enhancement in comparison to the conventional solid-state EC devices using TiO_2 nanoparticle film as a docking layer on a planar FTO electrodes. Meanwhile, the driving voltage can be reduced to less than 1.2 V and the devices show excellent reversibility and stability after nearly 4000 cycles. In perspective, the fast electron transport in the 3-dimensional conductive nanobead electrodes provides a feasible way to overcome

the persistence of vision for future sun-light readable and low-energy driven EC display technology as well as other electrochemical processes.

This approach is fundamentally advanced over current effort of alternating the morphology of docking materials from TiO_2 or ZnO nanoparticles to nanowires and other nanostructures. In particular, FTO has a high conductivity over $>10^3$ S/cm, (10^7 times greater than TiO_2 nanoparticle film) due to its high carrier concentration ($>10^{20}/cm^3$) and carrier mobility ($65\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).

The device configuration is illustrated in FIG. 1B. Hollow 3-dimensional FTO nanobeads (~200 nm in diameter) were sintered on a flat FTO glass as one electrode and another flat FTO glass as counter electrode. Diethyl viologen diiodine was chosen as the electrochromic material for the high stability of the viologen coloration state. The viologen molecules can be absorbed on both the inner and outer surfaces of the FTO nanobead electrode due to the small apertures (50 nm) on each FTO nanobead, which also allows the infiltration of the PMMA-P(VAc-MA)+LiClO₄-based sol-gel electrolyte, thereafter. The FTO nanobead electrodes were prepared by a morphology-controllable and template-assisted evaporative co-assembly method (Liu, F. Q., et al. "Three-dimensional conducting oxide nanoarchitectures: morphology-controllable synthesis, characterization, and applications in lithium-ion batteries" *Nanoscale* 2013, 5, 6422) and also briefly described below.

Preparation of FTO Nanobeads:

In a typical preparation process of FTO hollow nanobeads, 24 mg of $SnCl_2 \cdot 2H_2O$, 4.5 mg of NH_4F and 450 μl water were mixed and magnetically stirred for 2 hours. Then, 275 μl 200 nm PS suspension was added in the mixture, followed by stirring for 24 hours. 50 μl of the resulting suspension was spread on 1.0 inch \times 1.0 inch commercial FTO substrate with scotch tape to define the area. The samples were dried at room temperature overnight, following by 2 hours at 170° C., 3 hours at 340° C. and 2 hours at 450° C. with heating rate 1° C./min. This process yields approximately 15-20 μm 3-dimensional FTO hollow nanobead film. The samples were then treated at 300° C. in argon for 30 min to improve the electrical conductivity with temperature rising rate of 1° C./min.

Preparation of PMMA-P(VAc-MA)+LiClO₄-Based Sol-Gel Electrolytes

0.13 g of PMMA (polymethyl methacrylate) and 0.28 g copolymer of VAc/MA (vinyl acetate/methyl acrylate) was dissolved in 1 ml PC, 0.1 g LiClO₄ was added and stirred overnight.

Electrochromic Characterization

A square wave voltage was supplied by a function generator (Agilent 33220A) to power the EC devices. The voltage can be switched on from 0V to a given value between $\pm 5\text{V}$ within 50 ns. The periods of the alternating square wave voltage can be set for different values as needed such as 8 s, 4 s, 2 s, 1 s, 0.5 s and 0.3 s used in the tests.

Reflection vs. time of device was measured by the strip-chart function on UV-Vis spectrometer (Ocean Optic USB2000). The optic probe was placed on the sample holder and attached on the surface of the device.

Temperature dependent measurements were conducted by placing the EC device in a car cooler (Wagon Tech) that can adjust the temperature between 3-70° C. A thermocouple was taped on to the surface of the device to precisely record the actual sample temperature.

65 FIG. 2a shows the SEM top view of the FTO nanobead film. FIG. 2b is the cross-section of FTO nanobeads on ITO glass, showing that the thickness of FTO nanobead layer is

about 18 μm . FIG. 2c is a magnified SEM image of the FTO nanobeads with apertures of about 50 nm resulting from the release of gaseous species from the decomposed templating polystyrene nanobeads calcinated at 450° C. These openings offer the passages for the sol-gel electrolytes to pass through. FIG. 2d is the SEM image of FTO beads after viologens were absorbed. Our previous N_2 adsorption/desorption isotherms study shows that the BET surface area of 200 nm 3-dimensional FTO nanobeads is 53 m^2/g , and the measured mass per unit projected area of the FTO nanobead film with a thickness of 18 μm is $\sim 1 \text{ mg}/\text{cm}^2$. Thus, the surface roughness factor (effective surface area/projected substrate area) of this 18 μm thick FTO nanobeads film is over ~ 530 . The sheet resistance of the film was measured to be 27 Ω/square , indicating the excellent conductivity of the nanobead electrodes.

The device is driven by an alternating square-wave voltage supplied by a function generator, which is capable of alternating the polarity of voltage with a time resolution of 50 ns. The rate of the color change driven by the applied voltage, i.e. electrochromic effect, can be characterized by measuring the time-resolved reflectance (at a resolution of 20 ms) of the device at 580 nm, around which the first reduced state of viologen exhibits a wide absorption band. The lowest observed coloring voltage was $\sim 0.8 \text{ V}$, which is very close to the first reduction for most of alkyl substituted viologens $\text{V}^{2+} \rightarrow \text{V}^+$. FIG. 3a shows the real-time reflectance of the device at 580 nm vs. time driven by different square wave voltages ($\pm 0.9 \text{ V}$, $\pm 1.2 \text{ V}$ and $\pm 2.0 \text{ V}$). At -0.9 V (the negative voltage is defined as when the FTO nanobead electrode is negatively biased, and the flat counter electrode is positively biased) with periods of 8 s, 4 s, 2 s, and 1 s, the device shows a $\Delta 6.1\%$ reduction in reflection between fully de-colored and colored state. Further shortening the periods decreases the change of reflectance to 5% at period of 0.5 s. The device shows $\Delta 6.7\%$ and $\Delta 8\%$ reflectance change between de-colored and colored states at driving voltage of -1.2 V and -2 V , respectively. Although the absolute change of the reflectance is not high due to single-wavelength measurement, the device clearly shows the change of color from pale yellow to blue. Three video clips exhibit the visual effect of the rapid coloring-decoloring cycling driven by 0.9V square wave with periods of 100 ms, 200 ms and 600 ms, respectively.

FIG. 3b shows the response times of the coloring and de-coloring processes at $\pm 0.9 \text{ V}$. To assure a fair comparison with literature reported response times of the flat FTO electrode-based EC devices, the response times with respect to the 75%, 85% and 95% of the full color or de-color change was adopted. At -0.9 V , the response time is $\sim 270 \text{ ms}$ for reaching 75% coloring state and $\sim 400 \text{ ms}$ for reaching 75% de-coloring state, respectively. Even for 95% coloring and de-coloring state, the response time is only 540 ms and 861 ms, respectively, in contrast to the 2~3 s response time of the conventional EC devices using TiO_2 nanoparticles as the docking layer.

We also conducted temperature-dependent response time measurement in comparison with the temperature-dependent resistance of 3-dimensional FTO nanobead electrode and temperature-dependent resistance of the polymer electrolytes.

TABLE 1

Temp/K	Response Time vs Temperature defined at different change of percentage					
	T _c /ms 75% Co	T _d /ms 75% De	T _c /ms 85% Co	T _d /ms 85% De	T _c /ms 95% Co	T _d /ms 95% De
279.55	532	1040	803	1533	1230	2327
287.55	422	604	689	937	931	1216

TABLE 1-continued

Response Time vs Temperature defined at different change of percentage						
	T _c /ms 75% Co	T _d /ms 75% De	T _c /ms 85% Co	T _d /ms 85% De	T _c /ms 95% Co	T _d /ms 95% De
5	296.65	272	400	373	609	540
	307.65	216	429	332	385	422
	317.75	137	266	240	385	359
10	327.55	117	167	194	221	275

T_c: response time of coloring process

T_d: response time of decoloring process

Co: coloring

De: decoloring

15 This study provides insights on the rate-limiting steps of the EC process in the device. As shown in FIG. 4a, the Arrhenius plot of response time increase as temperature decreases at a slope of 2.99 (at 75% color change). In contrast, 20 the Arrhenius plot of resistance of polymer electrolytes increases as temperature decreases at a slope of 2.89, due to the decrease of ion mobility (i.e., kinetics) at lower temperature. Apparently, the resistance of the 3-dimensional FTO 25 nanobead electrode (slope of 0.56) has much less temperature dependence than the device response time and the resistance of polymer electrolytes. Since the slope of the Arrhenius plot of response time reflects the kinetic activation energy of the 30 EC process, while the overall EC process involves three steps, including electron transport in the FTO nanobead layer, ion transport in polymer electrolytes and the redox reaction of the 35 viologen. The comparison of the degree of the slopes of the Arrhenius plots indicates that the response time is mainly limited by the relatively slow ion transport in the electrolytes, instead of the electron transport in the FTO nanobead electrodes.

40 The reversibility of the device was further studied by applying cycling to the device at $\pm 0.9 \text{ V}$. After more than 3700 EC cycles (see FIG. 4b), no obvious decrease of performance was observed. The complete cycling graph is shown in FIG. 5.

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What is claimed is:

1. An electrochromic device, comprising:

(i) a conductive layer,
(ii) an electrochromic material, on the conductive layer
(iii) an electrolyte, on the electrochromic material, and
(iv) a counter-electrode, on the electrolyte,
wherein the conductive layer has a surface roughness factor (SRF) of at least 10,
the conductive layer comprises a semi-metal, and
the electrochromic device has a response time of at most 500 ms.

2. The electrochromic device of claim 1, wherein the electrochromic material is an organic electrochromic material.
3. The electrochromic device of claim 1, wherein the conductive layer has a SRF of at least 100.
4. The electrochromic device of claim 1, wherein the conductive layer is transparent.

5. The electrochromic device of claim 1, wherein the conductive layer comprises at least one member selected from the group consisting of fluorinated tin oxide, aluminum-zinc oxide, antimony-tin oxide and indium-tin oxide.
6. The electrochromic device of claim 1, wherein the electrochromic material is a viologen.

7. The electrochromic device of claim 1, further comprising a substrate, and the conductive layer is on the substrate.

8. The electrochromic device of claim 1, wherein the electrolyte comprises one member selected from the group consisting of liquid electrolytes and polymer electrolytes.
9. The electrochromic device of claim 1, wherein the electrolyte comprises one member selected from the group consisting of liquid electrolytes and ionic liquid electrolytes.

10. The electrochromic device of claim 1, wherein the electrolyte comprises a non-aqueous solvent.
11. The electrochromic device of claim 1, wherein the electrolyte comprises a salt.

12. The electrochromic device of claim 1, further comprising a transparent substrate, and the conductive layer is on the substrate,
wherein the electrochromic material is an organic electrochromic material,
the conductive layer has a SRF of at least 400, and
the conductive layer comprises at least one member selected from the group consisting of fluorinated tin oxide, aluminum-zinc oxide, antimony-tin oxide and indium-tin oxide.

13. The electrochromic device of claim 1, having a coloring voltage of at most 1V.

14. An electrochromic display, comprising a plurality of the electrochromic devices of claim 1.

15. The electrochromic display of claim 14, wherein the plurality of electrochromic devices comprises electrochromic materials having at least 3 different colors.

16. An electrochromic device, comprising:

(i) a conductive layer,
(ii) an electrochromic material, on the conductive layer
(iii) an electrolyte, on the electrochromic material, and
(iv) a counter-electrode, on the electrolyte,
wherein the conductive layer has a surface roughness factor (SRF) of at least 10,
the electrochromic material is not Ni oxide or hydroxide, and
the electrochromic device has a response time of at most 500 ms.

17. The electrochromic device of claim 16, wherein the conductive layer is transparent.

18. The electrochromic device of claim 16, wherein the electrochromic material is a viologen.

19. A process of preparing an electrochromic device, comprising:

forming a conductive layer, having a SRF of at least 10,
applying an electrochromic material onto the conductive
layer, and

preparing the electrochromic device using the conductive 10

layer and the electrochromic material,

wherein the electrochromic device comprises:

(i) a conductive layer,
(ii) an electrochromic material, on the conductive layer
(iii) an electrolyte, on the electrochromic material, and 15
(iv) a counter-electrode, on the electrolyte,

the conductive layer comprises a semi-metal, and

the electrochromic device has a response time of at most
500 ms.

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