

A hygroscopic hydrogelTechnical Field

The present invention relates to a hygroscopic hydrogel and a method of forming the same.

Background

Scavenging ambient energy sources in the environment to meet human energy demands either partly or fully has gained impetus to promote a sustainable society. Ambient sources typically used to date include solar energy, thermal energy and air flow.

Humidity in air has always been considered a waste resource and in fact, energy is often spent in reducing the humidity levels to levels suitable for human comfort. However, attempts to use ambient humidity in any useful physical form or energy are relatively sparse or utilise expensive and/or energy-intensive methods.

There is therefore a need for an improved hygroscopic material that is able to harness ambient humidity for energy harvesting at low cost and without using too much energy.

Summary of the invention

The present invention seeks to address these problems, and/or to provide an improved hygroscopic material which can absorb moisture from ambient humid atmosphere and transduce into different applications.

In general terms, the invention relates to a hygroscopic hydrogel that can be used to transduce ambient humidity into different kinds of signals. In particular, the hydrogel may exist in two states, namely a hydrated (H) state and a dehydrated (DH) state depending on the ambient humidity. The two states have distinct differences in optical, electrical, and electrochemical properties driven by the extent of moisture absorption by the hydrogel.

According to a first aspect, there is provided a hygroscopic hydrogel that switches between a hydrated state and a dehydrated state upon absorbing and desorbing water, respectively, the hydrogel comprising a non-stoichiometric oxide of a transition metal,

X, wherein the hydrogel in its dehydrated state has a molecular structure with a transition metal to oxygen (X:O) ratio of 1:1.1-1:1.5.

According to a particular aspect, a switch between the hydrated state and the dehydrated state of the hydrogel may causes a change in the optical, electrical and/or electrochemical properties of the hydrogel. In particular, the hydrogel may switch
5 between the hydrated state and the dehydrated state without external energy supply.

According to a particular aspect, the hydrogel in its dehydrated state may have an average optical transparency of $\geq 90\%$ in light having a wavelength of 390-700 nm. The hydrogel in its hydrated state may have an average incident infrared (IR) transmittance
10 of 50-65%.

According to another particular aspect, ionic conductivity of the hydrogel may increase as the hydrogel switches from the dehydrated state to the hydrated state. In particular, the hydrogel may be comprised in an electrochemical cell as an electrolyte.

According to a particular aspect, electrical resistivity of the hydrogel may decrease as the hydrogel switches from the dehydrated state to the hydrated state. In particular, the
15 hydrogel may be comprised in an electrical circuit as a conductive ink.

The transition metal, X comprised in the hydrogel may be any suitable transition metal. For example, X may be, but not limited to, zinc (Zn), copper (Cu), iron (Fe), silver (Ag), or a combination thereof. In particular, X may be Zn.

20 According to a particular aspect, the hydrogel may be porous. According to another particular aspect, the hydrogel may be amorphous.

According to a second aspect, the present invention provides a method of preparing the hygroscopic hydrogel according to the first aspect, the method comprising:

- mixing a transition metal acetate salt and an amino-alcohol in an alcohol to
25 form a precursor solution;
- adding deionised (DI) water to the precursor solution to form a mixture; and
- annealing the mixture at a pre-determined temperature for a pre-determined period of time to form the hydrogel.

In particular, the hydrogel formed by the method may be in a dehydrated state.

The transition metal acetate salt may be the acetate salt of any suitable transition metal. For example, the transition metal acetate salt may be, but not limited to, zinc acetate, copper acetate, iron acetate, silver acetate, or a combination thereof. In particular, the transition metal acetate salt may be zinc acetate.

According to a particular aspect, the amino-alcohol may be any suitable amino-alcohol for the purposes of the present invention. For example, the amino-alcohol may be, but not limited to, ethanolamine, propanolamine, or a combination thereof. In particular, the amino-alcohol may be ethanolamine.

According to a particular aspect, the alcohol may be any suitable alcohol for the purposes of the present invention. For example, the alcohol may be, but not limited to, ethanol, methanol, isopropanol, 2-methoxyethanol, or a combination thereof. In particular, the alcohol may be a glycol-ether. Even more in particular, the alcohol may be 2-methoxyethanol.

The annealing may be carried out for a suitable pre-determined period of time. For example, the pre-determined period of time may be 10-30 minutes.

The annealing may be carried out at a suitable pre-determined temperature. For example, the pre-determined temperature may be 30-80°C.

According to a particular aspect, the method may further comprise coating the mixture on a substrate prior to the annealing. The substrate may be any suitable substrate.

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1 shows a structure of a hydrogel according to one embodiment of the present invention in the dehydrated state;

Figure 2(a) shows a plot of the rate of water uptake by the gel when exposed to high humid (90% RH) conditions for a prolonged period of time; and Figure 2(b) shows a plot showing the reduction in RH in a confined space as the gel absorbs moisture from humid air;

- 5 Figure 3 shows a comparison of the water absorption capabilities of the hydrogel according to one embodiment of the present invention with other commercially available hygroscopic materials;

Figure 4(a) shows a plot of the adsorption energy vs number of water molecules. Figures 4(b) to (d) show the changes in the structure of the dehydrated hydrogel
10 according to one embodiment of the present invention on addition of 6 (Figure 4b), 11 (Figure 4c), 30 (Figure 4d) and 43 (Figure 4e) water molecules to the system;

Figure 5 shows the change in transmittance of the hydrogel according to one embodiment of the present invention from the dehydrated state (transparent) to the hydrated state (opaque) over time;

- 15 Figure 6 shows a plot showing the transmittance values for the hydrogel according to one embodiment of the present invention and that of a commercially available film;

Figure 7 shows a plot of the stability of the hydrogel according to one embodiment of the present invention after multiple water absorption/desorption cycles;

- Figure 8 shows a plot of the temperature variation of an enclosed glass container under
20 various conditions;

Figure 9 shows a plot of measured I/V characteristics of the hydrogel according to one embodiment of the present invention in DH and H states; and

Figure 10 shows a schematic representation of a setup for harvesting seawater from hydrated hydrogels according to one embodiment of the present invention.

25 Detailed Description

As explained above, there is a need for an improved material that is able to absorb water from the atmosphere and exhibit changes in physical properties. In particular, the present invention relates to a hygroscopic hydrogel which is able to transduce

ambient humidity into other useful signal/energy forms that can be used for a wide range of device applications, including tapping potable water.

The hygroscopic hydrogel of the present invention may absorb more than 400% of its own weight with water. In particular, the hygroscopic hydrogel of the present invention
5 allows easy desorption of water from the hydrogel without requiring an external energy source. This is in contrast to other hygroscopic materials like silica gel which require a lot of energy to desorb water. For example, heat build-up caused by a light of 1 sun intensity is sufficient to cause desorption of water from the gel, which is equivalent to about 1 kW/m².

10 According to a first aspect, there is provided a hygroscopic hydrogel that switches between a hydrated state and a dehydrated state upon absorbing and desorbing water, respectively, the hydrogel comprising a non-stoichiometric oxide of a transition metal, X, wherein the hydrogel in its dehydrated state has a molecular structure with a transition metal to oxygen (X:O) ratio of 1:1.1-1:1.5.

15 According to a particular aspect, the transition metal, X comprised in the hydrogel may be any suitable transition metal. X may be, but not limited to, zinc (Zn), copper (Cu), iron (Fe), silver (Ag), or a combination thereof. For example, X may be Zn, Cu, Fe, Ag, or a combination of Zn and Cu. In particular, X may be Zn.

The hydrogel may comprise a non-stoichiometric oxide of X, and wherein the hydrogel
20 comprises a structure with a X:O ratio of 1:1.1-1:1.5. In particular, the hydrogel may comprise a structure with a X:O ratio of 1:1.1, 1:1.2, 1:1.3, 1:1.4, 1:1.5. Even more in particular, the hydrogel may comprise a structure with a X:O ratio of 1:1.1.

According to a particular embodiment, the hydrogel may be a non-stoichiometric oxide of zinc, and wherein the hydrogel may comprise a structure with a Zn:O ratio of 1:1.1-
25 1:1.5. Even more in particular, the hydrogel may comprise a structure with a Zn:O ratio of 1:1.1. An example of the structure of the oxide of zinc hydrogel in its dehydrated state is shown in Figure 1. It can be seen from Figure 1 that the structure has no surface dangling bonds and comprises an open porous structure.

According to a particular aspect, the hydrogel may be porous. According to another
30 particular aspect, the hydrogel may be amorphous.

According to a particular aspect, a switch between the hydrated state and the dehydrated state of the hydrogel may causes a change in the optical, electrical and/or electrochemical properties of the hydrogel. In particular, the hydrogel may switch between the hydrated state and the dehydrated state without external energy supply.

- 5 For example, hydrogel in the hydrated state and the dehydrated state has distinct differences in optical, electrical, and electrochemical properties driven by the extent of moisture sorption. The hydrogel may initially be in the dehydrated state which, when exposed to ambient air of relative humidity (RH) of about 60%, absorbs water as high as 50% (by weight) within 2 hours to reach the hydrated state. On prolonged exposure
10 to a high humid atmosphere (about 90% RH), the hydrogel may absorb over 200% of its weight with water (see Figure 2(a)), which may be referred to as a saturated-hydrated state (H*). The consequent reduction in relative humidity in a confined environment is shown in Figure 2(b).

- Transition from the hydrated to dehydrated state may be achieved by simply exposing
15 the hydrogel to sunlight for a period of time. The period of time may be a period of time suitable for allowing the desorption of the water from the hydrogel. For example, the period of time may be about 15-25 minutes for a hydrogel having a surface area/weight ratio of about 120-180 cm²/g. Thus, water sorption and desorption in the hydrogel may be achieved purely by ambient energy sources, without any external energy supply.
20 However, if external energy is supplied, the water sorption and desorption in the hydrogel may be faster.

- In particular, the hydrogel of the present invention has a high water absorption capability and requires low temperature for water release. For example, the temperature required for water release may be about 45-60°C. This is in contrast to
25 hygroscopic materials in the field which have a low water uptake and have a high energy requirement for releasing the absorbed water. Figure 3 shows a comparison of water absorption capability of the hydrogel when compared to commercially available desiccants. Also used for comparison is ethanolamine, which is one of the starting materials used for synthesising the hydrogel. It can be seen that the hydrogel is much
30 more hygroscopic as compared to its starting materials.

Simulations of addition of water molecules to the DH hydrogel may be carried out by introducing 6, 11, 30 and 43 water molecules to a system consisting of 39 Zn and 42 O

atoms. Changes in the structure and the energy required for addition of water molecule with the number of water molecules are shown in Figure 4. It is evident from Figure 4(a) that as more and more water gets adsorbed to the DH hydrogel, the energy required for adsorption reduces and approaches zero (as number molecules introduced is increased to about 120). This shows that the water is physically adsorbed onto the hydrogel rather than hydroxylation which would require very high energy for desorption. Thus, it can be seen that desorption of water from the hydrogel requires only a minimal expense of energy.

As absorbing water from ambient air (in a confined volume) is a primary property of the hydrogel, there is a resultant change in the ambient humidity level in the confinement. Changes in: optical properties, such as visible light transmittance and infrared (IR) transmittance; electrical properties, such as electrical resistivity; and electrochemical properties, such as ionic conductivity, are results of moisture absorption which have been utilised in direct device realizations to harness humidity. Table 1 provides a summary of the applications of the hydrogel based on the hydrogel's primary water absorbing property.

Application	Property change	Stimulus	Response	DH	H
Chromogenic window	Optical (secondary)	Humidity	Transmittance (visible)	↑	↓
IR-blocking window	Optical (secondary)	Humidity	Transmittance (IR)	↑	↓
Conductive ink	Electrical (secondary)	Humidity	Electrical resistivity	↑	↓
Electrochemical cell	Electrochemical (secondary)	Humidity	Ionic resistivity	↓	↑
Dehumidifier	Primary	Humidity	Humidity	-	-

Table 1: Applications of the hydrogel based on the hydrogel's primary water absorbing property

Optical property change

(a) Chromogenic window

Current technologies in smart windows use either an electrochromic, thermochromic or gasochromic material and the switching from one optical state to another is driven by a change in stimulus like voltage, temperature or introduction of a gas. These designs require complex material processing techniques for fabrication or complicated designs.

In contrast, when using the hydrogel of the present invention in a chromogenic window, an optical transition from transparent to opaque state takes place by absorption of water from ambient air and the transition from opaque to transparent state can be achieved by exposing the hydrated hydrogel to sunlight. The hydrogel may be capable
5 of DH to H state transition under ambient humid air and H to DH states under sunlight, thus not requiring any additional energy. According to a particular aspect, the hydrogel in its dehydrated state may have an average optical transparency of $\geq 90\%$ in light having a wavelength of 390-700 nm (visible light regime).

Apart from exposing to sunlight, the transition from H to DH state may also be brought
10 about by any suitable means, such as resistive heating of the hydrogel. Since a major fraction of the absorbed water is physically absorbed, a small voltage, such as about 5 V may generate enough heat to induce the change from H to DH state. Accordingly, transition from transparent to opaque state and vice versa takes place at negligible energy requirement. Figure 5 shows the continuous change in the transmittance values
15 of the hydrogel from the dehydrated state to the hydrated state. In particular, application of a higher voltage may cause a faster transition from the H to the DH state.

According to a particular aspect, the hydrogel may be comprised on a glass substrate. For example, the hydrogel may be applied on a surface of a glass substrate. In particular, the hydrogel may be applied as a coating on a surface of a glass substrate.
20 Any suitable coating method maybe used for coating the hydrogel on a surface of a glass substrate.

In addition to the above, the reduction of humidity in a confined space may lead to a reduction or elimination in the use of dehumidifiers, thereby reducing the energy consumption in highly glazed buildings in which the hydrogel is applied.

As explained above, the hydrogel in the DH state may be transparent to visible light. Absorption of water by the hydrogel in the DH state leads to the formation of several air-liquid interfaces with pores which act as light scattering zones. Figure 6 shows visible light transmittance of the hydrogel in the DH and H states. An average transparency as high as 98.3% may be achieved in the DH state over the entire visible
25 spectrum, with a maximum transparency of 98.5% at $\lambda = 435$ nm.
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Figure 7 shows the results of an investigation on the stability and cyclic nature of the H to DH to H transition. One cycle was comprised of resistive heating of the hydrogel to convert it to the DH state with the DH hydrogel kept in an enclosed atmosphere maintained at RH = 70% for 15 minutes. The values of transmittance at 450 nm wavelength, taken at 1, 10, 25, 50, 75, 100, and 125 cycles indicate that the hydrogel has excellent reversibility with respect to transmittance in both transparent and opaque states.

(b) IR blocking

In addition to the switching from transparent to opaque states, the hydrogel in its hydrated state may have an average incident infrared (IR) transmittance of 50-65%. In particular, the average incident IR transmittance may be about 54%. This may drastically reduce the temperature build-up inside buildings comprising windows comprising the hydrogel. Accordingly, this may result in the reduction in the loads of energy intensive air conditioning units.

The reduction in the incident IR radiation may be attributed to the large volume of water absorbed by the hydrogel. As the absorbed water diffuses throughout the matrix of the hydrogel, the quantity of IR transmission decreases. Figure 6 shows the near IR transmittance of the hydrogel in H and DH states which is compared to the transmittance of a commercially available anti-glare sunscreen film used predominantly in buildings. The average near IR transmittance of the gel in the saturated H state is 53.68%, whereas the anti-glare film transmits 89.57% of the incident IR radiation. Accordingly, this property may be exploited to curtail temperature build-up resulting from radiative heating caused by incoming IR radiation from the sun.

To corroborate this effect further, an enclosed glass beaker was exposed to a tungsten halogen lamp under 3 conditions: without any coating, by coating a layer of the hydrogel in saturated H state along the insides of the beaker, and by using a commercial anti-glare sunscreen film. Figure 8 shows the rate of temperature increase in the aforementioned conditions. Since IR transmittance of the hydrogel in the H state was only 53.68%, a temperature difference of 7.2°C was observed with and without the hydrogel coating. Accordingly, with the hydrogel coated on a substrate surface, such as a glass surface of a building, the temperature rise within the building may be much

slower. Other applications in which the hydrogel may be applied include a surface of a vehicle.

Electrical and electrochemical property change

Exposure to atmospheric moisture also stimulates changes in electrical and electrochemical properties of the hydrogel. The resulting changes in these properties are manifested in the form of changes in electrical and ionic conductivities which enables utilization of the hydrogel for various electronic and electrical applications.

According to another particular aspect, ionic conductivity of the hydrogel may increase as the hydrogel switches from the dehydrated state to the hydrated state. In particular, the hydrogel may be comprised in an electrochemical cell as an electrolyte.

Transduction of humidity into changes in electrical properties were measured using IV curves for the gel. Figure 9 shows the IV curves of the hydrogel and pure ohmic contacts may be observed from the straight lines in both DH and H states of the hydrogel. An increase in slope of the I–V curve from the DH to H state indicates a reduction in resistance. From the slope of the I–V curves, the hydrogel in the DH state has a resistance of about 471.56 k Ω and upon water sorption the resistance reduces to about 25.5 k Ω . This resultant change may be attributed to the interaction of the absorbed water molecules with the transition metal ions present in the hydrogel.

An electrochemical cell was constructed using the hydrogel as electrolyte and zinc (Zn) and copper (Cu) as electrodes. Ionic conductivity of the electrolyte is a crucial parameter determining overall performance of an electrochemical cell. The electrodes were assembled on a flexible cellulose acetate sheet and the quasi-solid gel formed the electrochemical junction between the two electrodes.

When hydrogel in the DH state is used as the electrolyte, it has very low ionic conductivity which is reflected by a high electrochemical impedance. Humidity-induced electrochemical changes are apparent from the significant reduction in the charge transfer resistance and increase in ionic conductivity of the hydrogel. This increase in ionic conductivity and decrease in the charge transfer resistance of the hydrogel on water absorption enables the functionality of the hydrogel as an electrolyte for electrochemical cells.

The hydrogel may also be used in the fabrication of flexible printed circuits because its quasi-solid state facilitates easy laying of circuits on flexible substrates by drip coating/printing. According to a particular aspect, electrical resistivity of the hydrogel may decrease as the hydrogel switches from the dehydrated state to the hydrated state. In particular, the hydrogel may be comprised in an electrical circuit as a conductive ink.

An electrical circuit may be laid on a flexible cellulose acetate sheet by drip coating H* hydrogel. The H* state of the hydrogel, obtained by prolonged exposure of the hydrogel to high levels of humidity is a quasi-solid ionic solution having high electrical conductivities due to dissolution of ions in the absorbed water. To demonstrate the role of the hydrogel as a conductive ink, 3 LEDs were connected in an electrical circuit with the H* hydrogel forming the conductive path. On drip coating, the hydrogel formed a closed electrical circuit between the voltage source and the LEDs, thereby lighting them.

The hydrogel may be printed/drawn on any flexible biodegradable substrate and may be easily washed with acetic acid (or vinegar) enabling reusability of the substrate and minimizing solid electronic wastes and the associated energy demands for their disposal.

Desalination

Another application of the hydrogel according to the present invention may be in desalination. As water becomes a pressing issue throughout the globe, alternative methods to harvest freshwater have been on the rise. Desalination of seawater offers a much larger prospective owing to the abundance of seawater. However the current desalination methods like membrane processing via reverse osmosis are cost and energy intensive. Numerous other methods such as ion concentration polarization, salt removal using mono-layered materials are not viable to commercialize primarily because of the associated complexities in engineering mono-layered materials on a large scale. There is provided a simple humidification-dehumidification (HDH) approach using the hydrogel of the present invention to efficiently convert seawater to freshwater.

In particular, exposing the hydrogel to high humid conditions prevailing over the surface of water enables water uptake by the hydrogel. Exposure of the hydrogel to sunlight (1

sun condition) causes water desorption which can be condensed and collected without any additional energy requirement.

An example of a set-up which may be used for desalination of seawater is shown in Figure 10. In particular, multiple stacks of hydrogels in the H state may be placed in an enclosure, such as a glass enclosure to induce greenhouse heating. An external source may be used to simulate the condition, such as a halogen lamp. The glass when, exposed to sunlight of about 1 sun intensity or an external light source simulating 1 sun intensity, may heat up due to a greenhouse effect. In particular, when the greenhouse heating is induced, the multiple stacks of saturated hydrogels may be converted back into the dehydrated state, thereby releasing water vapour. This water vapour when it contacts the side walls of the glass container, where a heat transfer between the water vapour and the glass walls takes place, results in the condensation of the water vapour into water which may then be collected from the bottom of the outer glass container.

Chemical studies of the water desorbed from the hydrogel show that the water is clean and does not require any further purification. Current freshwater yield at lab scale is around 10 times the quantity of hydrogel used per day.

Raman spectrum of the water obtained desorbed from the hydrogel showed that there are no organic impurities present in the desorbed water. An elemental analysis carried out on the desorbed water showed that the ion concentrations are well within the limits specified by the World Health Organisation (WHO) (see Table 2).

Ions	Seawater (ppm)	Water desorbed from hydrogel (ppm)	Drinking water standard (WHO) (ppm)
Na	12400	0.46	<200
K	418	0.21	2.5-5
Ca	488	0.78	100
Mg	1443	0.04	
Zn	ND	0.94	3
F	ND	ND	1.5
Cl	21345	0.65	<200
Br	1.53	ND	N.A.
Nitrogen (Nitrates)	ND	2.87	50
Phosphates	ND	ND	N.A.
Sulphates	2250	0.5	<250

*ND: Not detected

Table 2: Elemental analysis comparison of water samples

As can be seen, the hydrogel of the present invention provides many uses and may be used in various applications. In addition to its ease of use, the hydrogel is also formed using a simple and scalable process.

According to a second aspect, the present invention provides a method of preparing the hygroscopic hydrogel according to the first aspect, the method comprising:

- mixing a transition metal acetate salt and an amino-alcohol in an alcohol to form a precursor solution;
- adding deionised (DI) water to the precursor solution to form a mixture; and
- annealing the mixture at a pre-determined temperature for a pre-determined period of time to form the hydrogel.

In particular, the hydrogel formed by the method may be in a dehydrated state.

The transition metal acetate salt may be any suitable acetate salt. In particular, the acetate salt may be that of any suitable transition metal, X, comprised in the hydrogel. For example, the transition metal acetate salt may be, but not limited to, zinc acetate, copper acetate, iron acetate, silver acetate, or a combination thereof. In particular, the transition metal acetate salt may be zinc acetate.

The amino-alcohol may be any suitable amino-alcohol for the purposes of the present invention. For example, the amino-alcohol may be, but not limited to, ethanolamine, propanolamine, or a combination thereof. In particular, the amino-alcohol may be ethanolamine.

- 5 The alcohol may be any suitable alcohol for the purposes of the present invention. According to a particular aspect, the alcohol may be a glycol-ether. For example, the alcohol may be, but not limited to, ethanol, methanol, isopropanol, 2-methoxyethanol, or a combination thereof. In particular, the alcohol may be 2-methoxyethanol.

The mixing may comprise mixing the transition metal acetate salt and amino-alcohol in
10 the alcohol solvent until all the transition metal acetate salt has dissolved. The mixing may be by any suitable means known in the art.

The mixing may further comprise sonicating the mixture of the transition metal acetate salt, amino-alcohol and alcohol for a period of time. In particular, the sonicating may aid in the dissolving of the transition metal acetate salt.

- 15 The adding of the DI water to the precursor solution may comprise adding a suitable amount of DI water to the precursor solution. In particular, DI water of an amount equal to the amount of the precursor solution is added to the precursor solution.

The annealing may be carried out under suitable conditions. According to a particular aspect, the annealing may be carried out for a suitable pre-determined period of time at
20 a suitable pre-determined temperature. For example, the pre-determined period of time may be about 10-30 minutes for a mixture having a surface area/weight ratio of about 120-180 cm²/g.

For example, the pre-determined period of time may be 10-30 minutes. In particular, the pre-determined period of time may be 12-28 minutes, 13-27 minutes, 15-25
25 minutes, 16-24 minutes, 17-23 minutes, 18-22 minutes, 19-20 minutes. Even more in particular, the pre-determined period of time may be about 20 minutes.

The pre-determined temperature may be 30-80°C. In particular, the pre-determined temperature may be 32-78°C, 35-75°C, 40-70°C, 45-65°C, 50-60°C, 52-55°C. Even more in particular, the pre-determined temperature may be about 50°C.

According to a particular aspect, the method may further comprise coating the mixture on a substrate prior to the annealing. The substrate may be any suitable substrate. In particular, the substrate may be any substrate which is able to withstand the annealing temperature. Even more in particular, the substrate may be fluorine doped tin oxide (FTO).

According to a particular aspect, the method may comprise:

- mixing zinc acetate, and ethanolamine in 2-methoxyethanol to form a precursor solution;
- adding DI water to the precursor solution to form a mixture; and
- annealing the mixture at a pre-determined temperature for a pre-determined period of time to form an oxide of zinc hydrogel.

In particular, the zinc acetate may have a concentration of about 0.7 M. In particular, the ethanolamine may have a concentration of about 0.7 M.

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention and that the embodiments are provided by way of illustration, and are not intended to be limiting.

Claims

1. A hygroscopic hydrogel that switches between a hydrated state and a dehydrated state upon absorbing and desorbing water, respectively, the hydrogel comprising a non-stoichiometric oxide of a transition metal, X, wherein the hydrogel in
5 its dehydrated state has a molecular structure with a transition metal to oxygen (X:O) ratio of 1:1.1-1:1.5.
2. The hydrogel according to claim 1, wherein the switch between the hydrated state and the dehydrated state causes a change in the optical, electrical and/or
10 electrochemical properties of the hydrogel.
3. The hydrogel according to claim 1 or 2, wherein the transition metal is: zinc (Zn), copper (Cu), iron (Fe), silver (Ag), or a combination thereof.
- 15 4. The hydrogel according to any preceding claim, wherein the hydrogel is porous.
5. The hydrogel according to any preceding claim, wherein the hydrogel is amorphous.
- 20 6. The hydrogel according to any preceding claim, wherein the hydrogel switches between the hydrated state and the dehydrated state without external energy supply.
7. The hydrogel according to any preceding claim, wherein the hydrogel in its dehydrated state has an average optical transparency of $\geq 90\%$ in light having a
25 wavelength of 390-700 nm.
8. The hydrogel according to any preceding claim, wherein the hydrogel in its hydrated state has an average incident infrared (IR) transmittance of 50-65%.
- 30 9. The hydrogel according to any of claims 1 to 7, wherein ionic conductivity of the hydrogel increases as the hydrogel switches from the dehydrated state to the hydrated state.

10. The hydrogel according to claim 9, wherein the hydrogel is comprised in an electrochemical cell as an electrolyte.

11. The hydrogel according to any of claims 1 to 7, wherein electrical resistivity of the hydrogel decreases as the hydrogel switches from the dehydrated state to the hydrated state.

12. The hydrogel according to claim 11, wherein the hydrogel is comprised in an electrical circuit as a conductive ink.

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13. A method of forming the hydrogel according to any of the preceding claims, the method comprising:

- mixing a transition metal acetate salt and an amino-alcohol in an alcohol to form a precursor solution;
- 15 - adding deionised (DI) water to the precursor solution to form a mixture; and
- annealing the mixture at a pre-determined temperature for a pre-determined period of time to form the hydrogel.

20 14. The method according to claim 13, wherein the transition metal acetate salt is: zinc acetate, copper acetate, iron acetate, silver acetate, or a combination thereof.

15. The method according to claim 13 or 14, wherein the amino-alcohol is: ethanolamine, propanolamine, or a combination thereof.

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16. The method according to any of claims 13 to 15, wherein the alcohol is: ethanol, methanol, isopropanol, 2-methoxyethanol, or a combination thereof.

17. The method according to any of claims 13 to 16, wherein the pre-determined period of time is 10-30 minutes.

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18. The method according to any of claims 13 to 17, wherein the pre-determined temperature is 30-80°C.

19. The method according to any of claims 13 to 18, wherein the method further comprises coating the mixture on a substrate prior to the annealing.

20. The method according to any of claims 13 to 19, wherein the hydrogel formed is
5 in a dehydrated state.