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(54) Title: A CONDUCTING ELECTROCHROMIC COMPOSITE OF METALLIC NANOWIRES AND MULTI-COLOURED THERMOCHROMIC MATERIALS

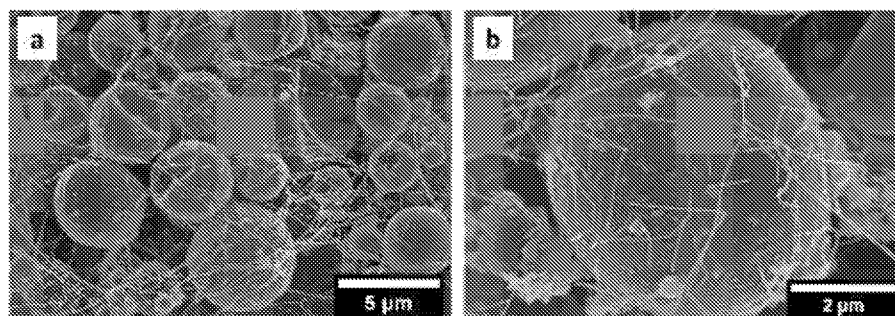


FIGURE 2

(57) Abstract: The invention pertains to a conducting electrochromic composite comprising of metallic nanowires, thermochromic material, and optionally a conducting polymer. Further, the thermochromic material is selected from a material that reversibly changes its colour with temperature. The conducting electrochromic composite comprises 4-6 wt% of metallic nanowires, 2-6 wt% of thermochromic material, and optionally 10-15 vol% of the conducting polymer. The deposition of the conducting electrochromic composite on the surface is one of drop-casting, dip coating, brush painting, spin coating, rod-coating, printing, or pen writing.



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A CONDUCTING ELECTROCHROMIC COMPOSITE OF METALLIC NANOWIRES AND MULTI-COLOURED THERMOCHROMIC MATERIALS

5 **FIELD OF INVENTION:**

The invention relates to composite of electrochromic material and specifically a composite which is flexible exhibiting both electrochromic and thermochromic properties.

10 **BACKGROUND:**

Electrochromism refers to a phenomenon where the colour of a material changes with the application of an electric field. The change is reversible and the material will return to its original colour once the field is removed. The colour change can be either between transparent and opaque states or between any two visible coloured states.

15 Electrochromism is widely reported in metal oxides such as tungsten, molybdenum, titanium, nickel, and niobium oxides because of the electrochemical oxidation and reduction of the transition metal ion. But the deposition of these materials is highly complex, not cost-effective, and cannot be used in flexible applications. Conducting polymers such as polypyrrole, PEDOT, and polyaniline show electrochromism, but

20 with limited colour variations. Many electrolyte-based and multi-layer electrochromic devices are available, but their fabrication is highly complex, expensive, and with limited flexible properties. A thermochromic material is the one that reversibly changes its colour with temperature. Some organic materials exhibit thermochromism, they are coloured in cooled state and changes to white or colourless once heated above

25 a transition temperature. Alterations in the intramolecular bond chains with temperature, which in turn changes the light absorption, is the cause of this colour change.

The existing conventional electrochromic devices require a multi-layered structure

30 consisting of the colour changing layer(s) and the electrode layers for supplying charge. They are fabricated by using complex deposition techniques and generally not flexible. Further, electrochromic devices available in the art are electrolyte-based and depend on the change in valence state for colour change. Thus, there is a need for a

cost-effective electrochromic material/composite which is relatively easy to manufacture and of low-cost, flexible, easy to cast and drop, and being a conducting material.

5 **OBJECT OF THE INVENTION:**

An object of the invention is for a conducting electrochromic composite comprising of metallic nanowires (NW), thermochromic material and optionally a conducting polymer.

- 10 Another object is for the conducting electrochromic composite as a powder or a liquid which is flexible and the deposition of the composite on the surface is one of drop-casting, dip coating, brush painting, spin coating, rod-coating, printing, or pen writing.

DESCRIPTION OF DRAWINGS AND FIGURES:

- 15 FIGURE 1 depicts the properties of the thermochromic powder. (a) shows the particle size distribution on a semilog scale and (b) shows the DSC properties that confirm the reversible change in the phases with temperature.

- FIGURE 2 is the photomicrograph of SEM image of the nanocomposite ink, made of
20 silver nanowires and the thermochromic material at different magnifications. A continuous network of NWs covering the thermochromic particles can be seen.

- FIGURE 3 depicts (a) The X-ray diffraction (XRD) pattern of the composite material, with and without applied voltage. (b) The phase change can be seen in the lower angles
25 of the diffraction plot.

- FIGURE 4 depicting the XRD pattern of the thermochromic powder, the composite film without voltage and with voltage. The phase of the composite film is observed to be changing with voltage.

30

- FIGURE 5 depicts the XRD peaks of the electrochromic material and peak fit corresponding to the Ag NW and the thermochromic material.

FIGURE 6 depicts the drop cast patterns of the thermochromic nanowire composite ink in different colours. The colour changes to white with voltage supply and returns to its original colour once the voltage is removed.

5 **DEFINITIONS:**

Thermochromism: Thermochromism is the phenomenon of reversible change in the colour of a material with a change in temperature.

Electrochromism: Electrochromism is the phenomenon of reversible colour change with application of a voltage or an electric field.

10 **Joule Effect:** Joule effect is the heating of resistive material with the passage of the electric current. The heat produced depends on the electric current flows through the material and its resistance.

Phase change: Phase change refers to the change in the phase (solid, liquid or gas) of the material without any change in the chemical composition.

15

DETAILED DESCRIPTION:

Accordingly, the aspect of the invention is for a conducting electrochromic composite comprising of metallic nanowires, thermochromic material and optionally a conducting polymer.

20

In an aspect the metallic nanowire is selected from tungsten, molybdenum, titanium, nickel, or niobium and preferably the metallic nanowire is silver.

In an aspect the thermochromic material is selected from a material that reversibly
25 changes its colour with temperature.

The thermochromic material used in the preparation of the conducting electrochromic composite is a powder or a liquid.

30 In another aspect the thermochromic material is of a single colour electrochromic material by choosing the right thermochromic powders. Multiple thermochromic powders are mixed to make a variety of colour gradients.

The thermochromic powder is purchased from Americos Chemicals Private Ltd., and is a mixture of crystal violet lactone, a leuco dye, bisphenol A, a colour developer, and tetradecanol, a low melting co-solvent. It works with any thermochromic powder from other commercial establishments such as Sigma Aldrich, Atlanta Chemical Engineering, and LCR Hall Crest.

In another aspect the conducting electrochromic composite optionally comprises of conducting polymer and is selected from polymers such as polypyrrole, PEDOT, PSS and polyaniline.

10

The conducting electrochromic composite comprises 4-6 wt% of metallic nanowires, 2-6 wt% of thermochromic material, and optionally 10-15 vol% of the conducting polymer.

15 In an aspect the temperature of the thermochromic material of the conducting electrochromic composite is a function of voltage.

In an aspect the conducting electrochromic composite is a function of Joule heating of metallic NWs and a concomitant colour change of the thermochromic material.

20

Further the conducting electrochromic composite is a dispersion.

The deposition of the conducting electrochromic composite on the surface/substrate is one of drop-casting, dip coating, brush painting, spin coating, rod-coating, printing, or pen writing.

25

The deposition of the conducting electrochromic composite on the surface/substrate is of a single layer.

After deposition, the substrate with the conducting electrochromic composite material is annealed at a temperature between 80 to 150 °C for 1 h for the solvent evaporation.

30

The conducting electrochromic composite deposition is on any surface/substrate such as photo paper, PET, or plastic sheets.

5 The composite is synthesized as a dispersion in a solvent or solvent mixture and selected from one of the alcohols, such as methanol, ethanol, and isopropyl alcohol, or polyols, such as ethylene glycol, poly-ethylene glycol, glycerol, propanediol, and dipropylene glycol, or ketones, such as acetone, or deionized water.

10 The conducting electrochromic composite has good flexible properties and is functional even under curved or bent conditions. The material is suitable to make low-cost flexible colour displays for interactive electronic-readers, digital posters, and flexible digital signboards.

15 The differential scanning calorimetric (DSC) plot of the thermochromic powder shows a peak at 35°C while heating and at 25°C while cooling (Figure 1B), each corresponds to the change in colour while heating and reobtaining the original colour upon cooling.

20 In an aspect the amount of metallic NWs is selected to be sufficient to form a continuous electrical network through which current can flow. Greater the concentration of NWs, lower the resistance and hence a larger amount of current flows and cause the temperature of the NWs to increase because of the Joule effect. This increases the temperature of the surrounding thermochromic particles in the composite. The uniform dispersion of the thermochromic material in the composite results in colour change on a macroscopic scale. The concentration of thermochromic material is selected that which determines the visibility of the colour change. In an aspect the same effect is seen in blends of thermochromic materials.

30 A conducting polymer such as PEDOT:PSS is added further, and improves the electrical, thermal, and mechanical functionalities of the material. After deposition, the substrate with the conducting electrochromic composite material is annealed at a temperature between 80 to 150 °C for 1 h for the solvent evaporation.

In an aspect the silver nanowires have an average length of around 30 μm and hence an individual nanowire span the length of the thermochromic particle and also makes electrical contacts with each other as shown by the SEM images (Figure 2). The continuity of the NW network is highly crucial for good conductivity. The particle size
5 of thermochromic material plays a crucial role in the rate of change in phase, smaller the particles quicker will be the transformation.

X-ray diffraction (XRD) pattern of the composite material with and without an applied voltage (Figure 3) shows peaks at 38, 44, 64, 77, and 81°. The remaining peaks
10 correspond to the characteristic peaks of the thermochromic material. When a voltage is applied across the material, it is observed that the thermochromic peaks become broadened and diffused together in the XRD pattern, which is because of the change from the ordered phase to the disordered phase, due to a change in the hybridization of the orbitals.

15 Thermochromic materials are non-conducting and hence will not respond to a potential or an electric field. Metallic NWs are highly conducting and hence their temperature will increase with under a small potential due to Joule heating. By forming a composite with metallic NWs, the temperature of the thermochromic material is controlled as a
20 function of voltage and thereby can change the material colour. Figure 5 shows the XRD pattern of the thermochromic material. When Ag NWs are added, extra peaks are observed at 38, 44, 64, 77, and 81° correspond to the FCC structure of the silver (standard reference JCPDS file No. 04-0783). There was no change in the characteristic peaks of thermochromic powder which confirms that the NWs are not
25 altering any structural properties of the thermochromic material. The material is tested by applying a voltage and a reversible colour change is observed. When the temperature increases, the peaks corresponding to the thermochromic material became broadened in the XRD pattern. This is because of the change of the material from an ordered phase to a disordered phase, due to a change in the hybridization of the orbitals.
30 There is no change in the metallic NWs during this process.

The XRD peaks of the Ag NWs, thermochromic materials and the conducting electrochromic composite as depicted in figure 5 shows that the composite is synergistic

composite of the metallic nanowires and the thermochromic material and the following table provides the peak intensities.

Table showing the fitted XRD peaks of the Ag NWs and thermochromic materials

5

Fitted peak	Material
81.5 ± 0.0	Ag NW peaks
77.4 ± 0.1	
64.4 ± 0.1	
44.2 ± 0.0	
38.3 ± 0.0	
23.9 ± 0.0	Thermochromic material peaks
21.7 ± 0.0	
20.5 ± 0.0	
19.9 ± 0.0	

EXAMPLES:

10 The invention is described in detail in the above figures and description, and the following examples below are provided as an illustration and are not intended to restrict the scope of the invention in any manner. Any embodiments that may be apparent to a person skilled in the art are deemed to fall within the scope of the present invention.

15

EXAMPLE 1:

Preparation of the Composite Material:

The silver NWs were cleaned in ethanol, isopropyl alcohol, and deionized water sequentially before dispersing in water, the final solvent. 5 wt. % of NWs were dispersed in the solution. 4 wt. % of leuco dye based thermochromic powder (a mixture of crystal violet lactone, a leuco dye, bisphenol A, a colour developer, and tetradecanol, a low melting co-solvent), purchased from Americos Chemicals Private Ltd., was added in this dispersion. Optionally, 1 wt. % PEDOT:PSS dispersed in water, was added to the prepared NW dispersion in a 12 vol. % ratio. The dispersion was sonicated for 10 mins for the proper mixing of the components. The composite dispersion obtained from the above is deposited on the photopaper deposited by drop.

25

After deposition, the substrate is annealed, at 100 °C for 1 h for the solvent evaporation.

EXAMPLE 2:

5 The silver NWs were cleaned in ethanol, isopropyl alcohol, and deionized water sequentially before dispersing in isopropyl alcohol, the final solvent. 5 wt. % of NWs were dispersed in the solution. 5 wt. % of leuco dye based thermochromic powder (a mixture of crystal violet lactone, a leuco dye, bisphenol A, a colour developer, and tetradecanol, a low melting co-solvent), purchased from Americos Chemicals Private
10 Ltd., was added in this dispersion. Optionally, 1 wt. % PEDOT:PSS dispersed in water, was added to the prepared NW dispersion in a 12 vol. % ratio. The dispersion was sonicated for 10 mins for the proper mixing of the components. The composite dispersion obtained from the above is deposited on the glass substrate deposited by spin coating. After deposition, the substrate is annealed, at 150 °C for 1 h for the
15 solvent evaporation.

EXAMPLE 3:

The silver NWs were cleaned in ethanol, isopropyl alcohol, and deionized water sequentially before dispersing in poly-ethylene glycol, the final solvent. 6 wt. % of
20 NWs were dispersed in the solution. 6 wt. % of leuco dye based thermochromic powder, purchased from Americos Chemicals Private Ltd., (a mixture of crystal violet lactone, a leuco dye, bisphenol A, a colour developer, and tetradecanol, a low melting co-solvent) was added in this dispersion. Optionally, 1 wt. % PEDOT:PSS dispersed in water, was added to the prepared NW dispersion in a 12 vol. % ratio. The dispersion
25 was sonicated for 10 mins for the proper mixing of the components. The composite dispersion obtained from the above is deposited on the PET sheet deposited by rod coating. After deposition, the substrate is annealed, at 100 °C for 1 h for the solvent evaporation.

EXAMPLE 4:

30 The composite material is subjected to XRD. X-ray diffraction (XRD) was performed in X'pert Pro PANalytical diffractometer operated at 45 kV. Figure 5 shows the

XRD pattern of the composite electrochromic material. The XRD peaks can be deconvoluted into Ag NW peaks, observed at 38, 44, 64, 77, and 81° and the remaining as that corresponds to the thermochromic material. There was no change in the characteristic peaks of thermochromic powder which confirms that the NWs are not altering any structural properties of the thermochromic material. The material is tested by applying a voltage and a reversible colour change is observed. When the temperature increases, the peaks corresponding to the thermochromic material became broadened in the XRD pattern, as shown in figure 3. This is because of the change of the material from an ordered phase to a disordered phase, due to a change in the hybridization of the orbitals. There is no change in the metallic NWs during this process.

ADVANTAGES:

The composite is relatively easy to manufacture and of low-cost.

15 The final material is prepared in a dispersion form, which can be easily applied over the substrate using any of the conventional solution-based deposition techniques such as drop-casting, dip coating, brush painting, spin coating, rod-coating, printing or pen writing.

A single layer deposition is sufficient, without needing any complex multi-step deposition processes currently in use to fabricate electrochromic devices.

20 The dispersion has very low post-deposition annealing requirements, typically 100 °C for 1 h. Support multiple colours and can be controlled by the applied voltage.

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The claim:

1. A conducting electrochromic composite comprising of metallic nanowires, thermochromic material, and optionally a conducting polymer.
2. The conducting electrochromic composite as claimed in claim 1, wherein the metallic nanowire is silver.
3. The conducting electrochromic composite as claimed in claim 1, wherein the thermochromic material is selected from a material that reversibly changes its colour with temperature.
4. The conducting electrochromic composite as claimed in claim 3, wherein the thermochromic material is a powder or a liquid.
5. The conducting electrochromic composite as claimed in claim 4, wherein the particle size of the thermochromic material is $5 \pm 2 \mu\text{m}$.
6. The conducting electrochromic composite as claimed in claim 1, wherein the thermochromic material is of a single colour or a combination of colours.
7. The conducting electrochromic composite as claimed in claim 1, wherein the thermochromic material is selected from any leuco based thermochromic powder.
8. The conducting electrochromic composite as claimed in claim 1, wherein the conducting polymer is selected from polymers such as polypyrrole, PEDOT, and polyaniline.
9. The conducting electrochromic composite as claimed in claim 1, wherein the composite comprises 4-6 wt% of metallic nanowires, 2-6 wt% of

thermochromic material, and optionally 10-15 vol% of the conducting polymer.

5 10. The conducting electrochromic composite as claimed in claim 1, wherein the temperature of the thermochromic material is a function of voltage.

11. The conducting electrochromic composite as claimed in claim 1, wherein the temperature of the metallic nanowire is a function of Joule effect.

10 12. The conducting electrochromic composite as claimed in claim 1, wherein the composite is a dispersion.

15 13. The conducting electrochromic composite as claimed in claim 10, wherein the deposition of the composite on the surface is one of drop-casting, dip coating, brush painting, spin coating, rod-coating, printing, or pen writing.

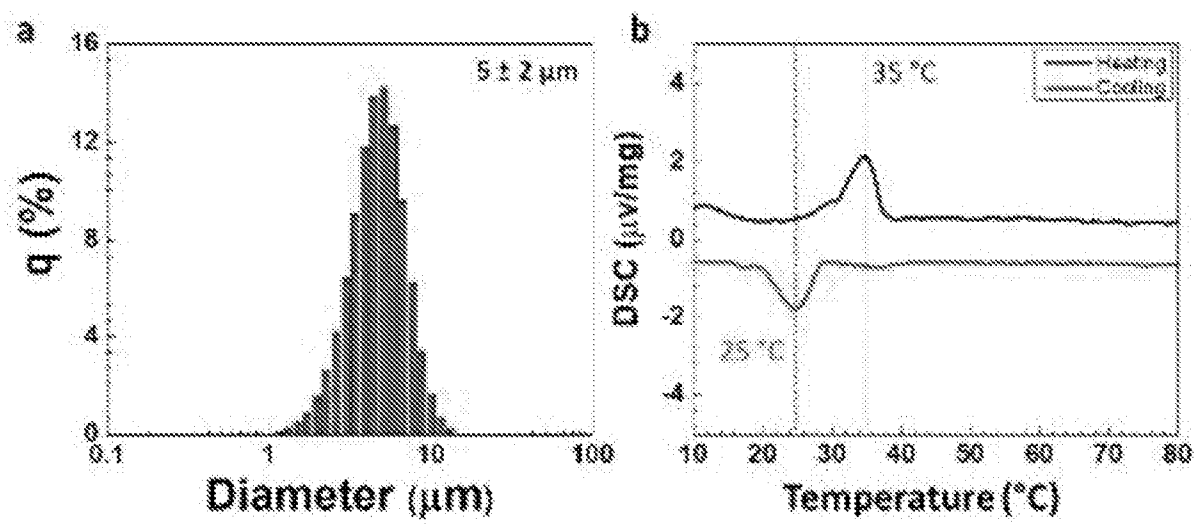


FIGURE 1

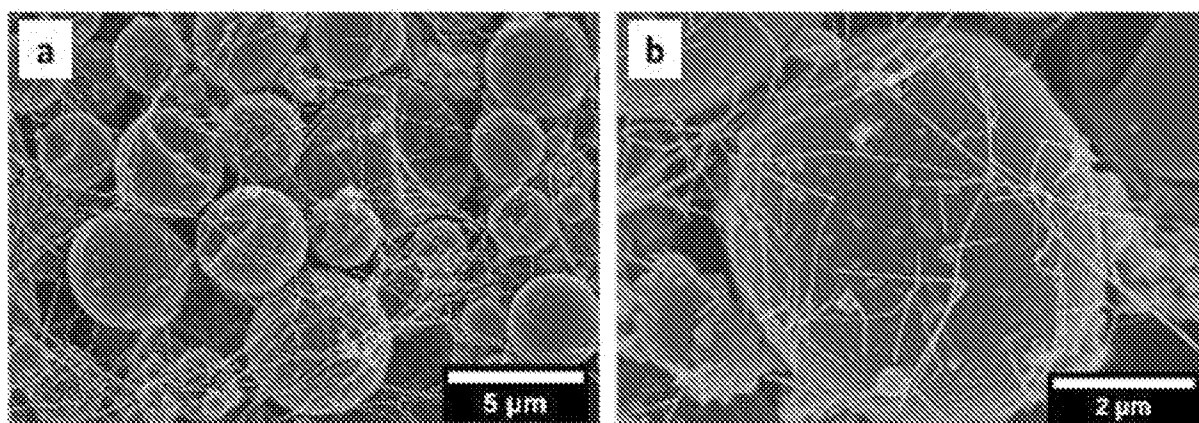


FIGURE 2

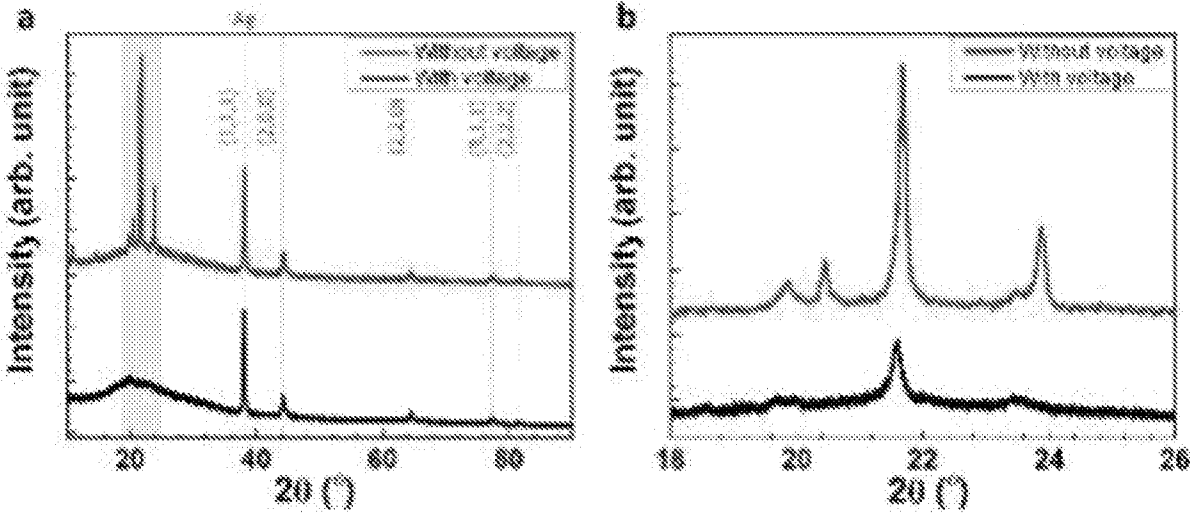


FIGURE 3

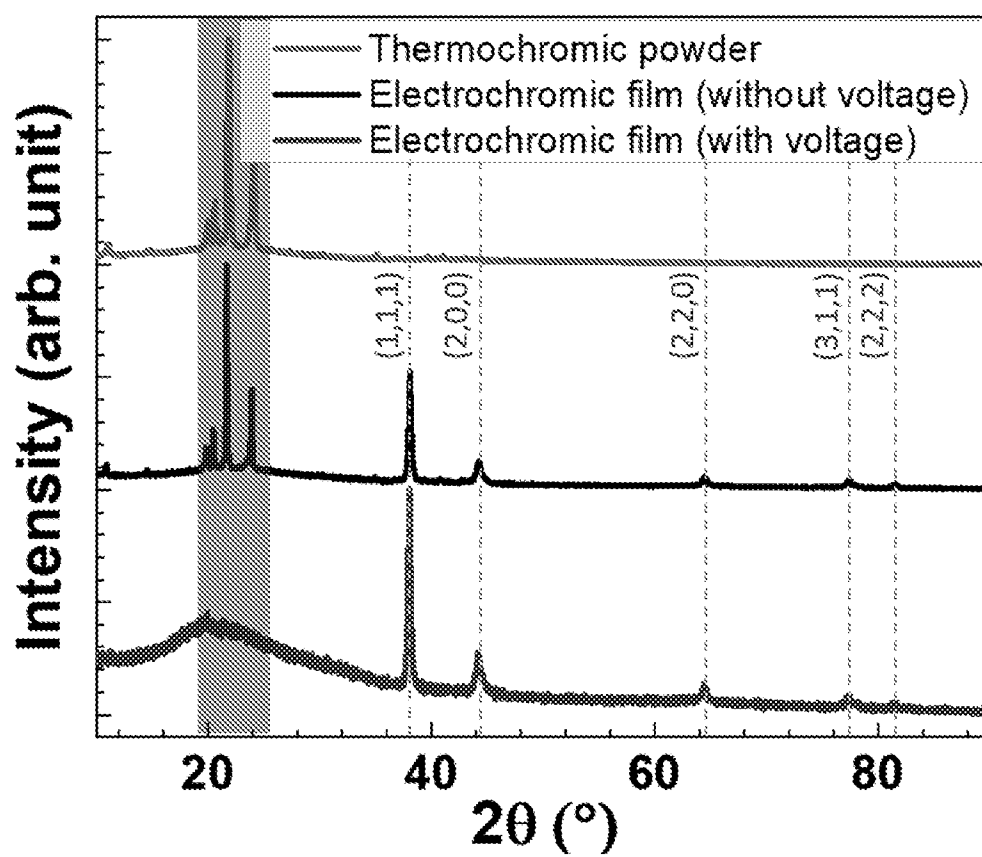


FIGURE 4

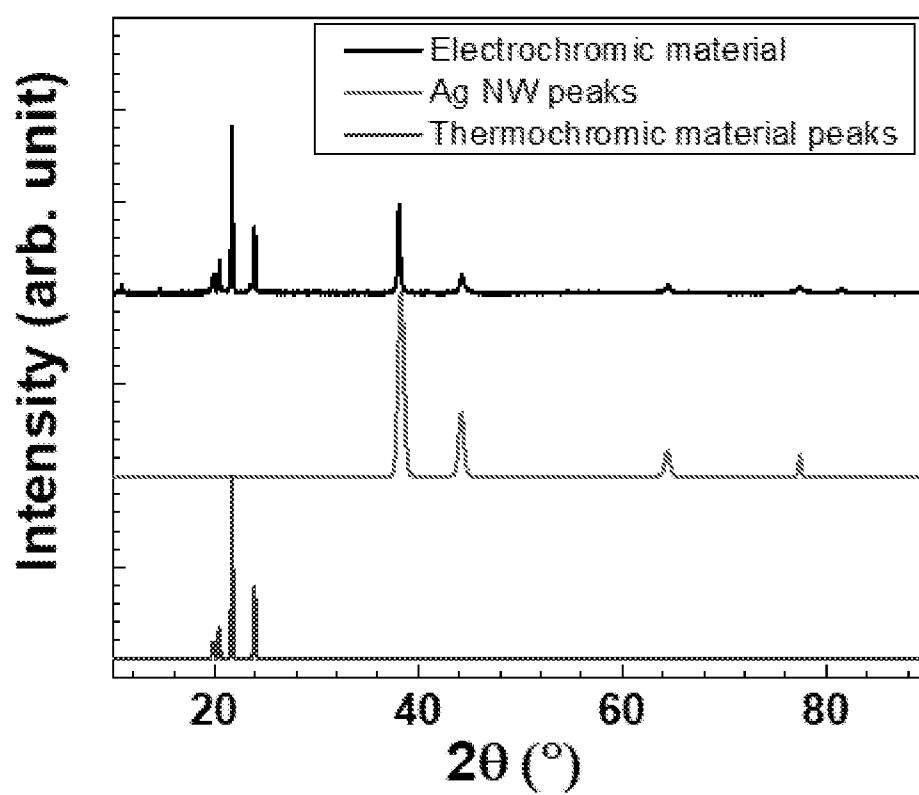


FIGURE 5

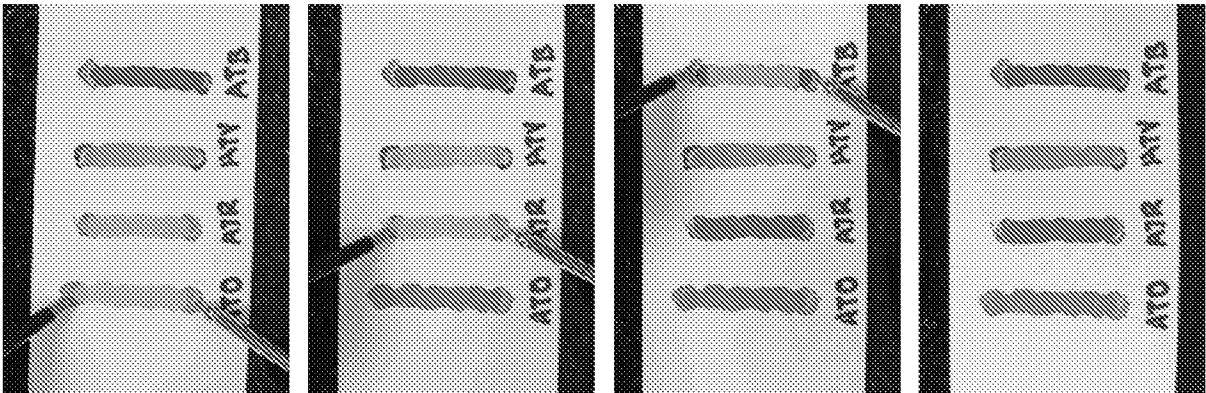


FIGURE 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2021/050569

A. CLASSIFICATION OF SUBJECT MATTER
B32B15/02 Version=2021.01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B32B15/02

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSeer, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO2018007355 (A1) BASF SE 11 Jan 2018 page 16: line 15- page 17: line 15; Claims 1-4, 6-10	1-2, 12
Y	Whole document -----	3-11, 13
Y	US20110217544 (A1) INNOVA DYNAMICS INC- 08 Sep 2011 paragraph [0005]- [0006]; paragraph [0052] paragraph [0179], Claims 1 and 24	3-11, 13

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IN2021/050569

Citation	Pub.Date	Family	Pub.Date
WO 2018007355 A1	11-01-2018	TW 201811558 A1	01-04-2018
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