

CONDUCTIVE PAPER AND METHOD OF FORMING THE SAME

Cross-reference to Related Application

[0001] This application claims the benefit of priority of United States patent application No. 61/892,108, filed 17 October 2013, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[0002] Various aspects of this disclosure relate to conductive papers and methods of forming the same.

Background

[0003] Cellulose is one of the most common organic material on earth. Paper is a product made of cellulose that is widely used. It has advantages such as low cost, flexibility and porosity, which allow it to be widely used. Recently, paper has been used for electronics applications, and electronic elements such as transistors have been fabricated on paper as a substrate.

Summary

[0004] In various embodiments, a method of forming a conductive paper may be provided. The method may include forming a first layer over a membrane, the first layer including an electrically conductive nanostructured material. The method may also include forming a second layer, the second layer including cellulose material, over the first layer so that an intermediate layer including the electrically conductive nanostructured material and the cellulose material is formed between the first layer and the second layer by interspersing of the electrically conductive nanostructured material between the cellulose material, thereby forming a stacked structure including

the first layer, the second layer and the intermediate layer. The method may further include separating the stacked structure from the membrane to form the conductive paper.

[0005] In various embodiments, a conductive paper may be provided. The conductive paper may include a first layer including an electrically conductive nanostructured material. The conductive paper may also include a second layer over the first layer, the second layer including a cellulose material. The conductive paper may further include an intermediate layer between the first layer and the second layer, the intermediate layer including the electrically conductive nanostructured material interspersed between the cellulose material.

Brief description of the drawings

[0006] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

FIG. 1 is a schematic showing a conductive paper according to various embodiments.

FIG. 2 is a schematic illustrating a method to form a conductive nanopaper according to various embodiments.

FIG. 3A is a photo of a transparent nanopaper according to various embodiments.

FIG. 3B is a schematic showing a setup to measure a transparency of a substrate according to various embodiments.

FIG. 3C is a scanning electron microscopy image of a nanopaper according to various embodiments.

FIG. 3D is a graph of counts against diameter (nm) showing the diameter distribution of a sample of cellulose nanofibrils according to various embodiments.

FIG. 4A is a flowchart showing a method of forming a conductive nanopaper according to various embodiments.

FIG. 4B is a schematic illustrating the method shown in FIG. 4A according to various embodiments.

FIG. 5A shows a graph of stress (MPa) against strain (%) of a conductive nanopaper formed according to various embodiments.

FIG. 5B shows a field emission scanning electron microscopy (FESEM) image of cellulose nanofibrils (CNFs) according to various embodiments.

FIG. 6A shows a graph of transmittance (%) against wavelength (nm) of various samples at about zero mm from an integrating sphere detector ($d = 0$ mm).

FIG. 6B shows a graph of transmittance (%) against wavelength (nm) of various samples at about twenty mm from an integrating sphere detector ($d = 20$ mm).

FIG. 6C shows a graph of transparency (%) against distance (mm) measured for light of wavelength of about 600 nm.

FIG. 7A shows a photo of a nanopaper according to various embodiments held to the background.

FIG. 7B shows a photo of a nanopaper according to various embodiments held at a distance from the background.

FIG. 7C shows a photo of a nanopaper treated with PDMS according to various embodiments held to the background.

FIG. 7D shows a photo of a nanopaper treated with PDMS according to various embodiments held at a distance from the background.

FIG. 8A is a photo showing the resistance measurement of a conductive nanopaper formed by a method including depositing electrically conductive nanostructured material first, followed by depositing the cellulose material on the electrically conductive nanostructured material according to various embodiments.

FIG. 8B is a photo showing the resistance measurement of a conductive nanopaper formed by a method including depositing the cellulose material first, followed by depositing the electrically conductive nanostructured material on the cellulose material according to various embodiments.

FIG. 9A is a schematic illustrating introduction of a plurality of droplets including the electrically conductive nanostructured material to the membrane according to various embodiments.

FIG. 9B is a schematic further illustrating the selective layering approach according to various embodiments.

FIG. 10A is a schematic showing a first group of droplets being deposited according to various embodiments.

FIG. 10B is a schematic showing a second group of droplets being deposited according to various embodiments.

FIG. 10C is a schematic shows a third group of droplets being deposited according to various embodiments.

FIG. 10D is a schematic showing a fourth group of droplets being deposited according to various embodiments.

FIG. 11 is a box plot of sheet resistance (ohms/square) of multiple point measurements on a conductive nanopaper formed with the selective layering approach according to various embodiments.

FIG. 12A is a schematic showing a membrane being provided according to various embodiments.

FIG. 12B is a schematic showing a plurality of droplets being deposited on or introduced to the membrane according to various embodiments.

FIG. 12C is a schematic showing nanocellulose material being vacuum filtered on the Ag nanowire droplets according to various embodiments.

FIG. 12D is a schematic showing a stacked structure including the nanocellulose material and the silver (Ag) nanowire droplets being dried according to various embodiments.

FIG. 12E is a schematic showing the stacked structure being peeled off from the membrane according to various embodiments.

FIG. 12F is a schematic showing a conductive nanopaper including the silver (Ag) nanowires and the nanocellulose material according to various embodiments.

FIG. 13A is a photo of an electrochromic paper being applied with a potential difference of about +0.3 V relative to a silver/silver chloride (Ag/AgCl) reference electrode according to various embodiments.

FIG. 13B is a photo of the electrochromic paper (shown in FIG. 13A) being applied with a potential difference of about -0.7 V relative to the silver/silver chloride (Ag/AgCl) reference electrode according to various embodiments.

FIG. 14A is a field emission scanning electron microscopy (FESEM) image of a conductive nanopaper according to various embodiments.

FIG. 14B is a field emission scanning electron microscopy (FESEM) image of an electrochromic paper including tungsten oxide on the conductive nanopaper according to various embodiments.

FIG. 14C is a magnified field emission scanning electron microscopy (FESEM) image showing tungsten oxide (WO_3) nanoparticles anchored to a cellulose nanofibril according to various embodiments.

FIG. 15A is a schematic showing forming a first layer on a membrane according to various embodiments.

FIG. 15B is a schematic showing forming a second layer over the first layer according to various embodiments.

FIG. 15C is a schematic showing the stacked structure being separated from the membrane according to various embodiments.

FIG. 15D is a schematic showing electrodes on the stacked structure according to various embodiments.

FIG. 16A is a schematic showing a photodetector according to various embodiments.

FIG. 16B is a photo showing the photodetector illustrated in FIG. 16A being held at a distance from a background.

FIG. 16C is a photo showing the photodetector shown in FIG. 16B on the background.

FIG. 16D is a field emission scanning electrode microscopy image (FESEM) of the disulphide (MoS_2) nanosheets according to various embodiments.

FIG. 16E is a magnified field emission scanning electrode microscopy image (FESEM) of the disulphide (MoS_2) nanosheets according to various embodiments.

FIG. 16F is a further magnified field emission scanning electrode microscopy image (FESEM) of the disulphide (MoS_2) nanosheets according to various embodiments.

FIG. 17A is a graph of current (nA) as a function of voltage (V) measured under light condition and under dark condition according to various embodiments.

FIG. 17B is a graph of current (nA) as a function of time (s) according to various embodiments.

FIG. 17C is a graph of normalized current (in arbitrary units or a.u.) as a function of time (s) for set and reset operations according to various embodiments.

Detailed description

[0007] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced.

[0008] The word "exemplary" is used herein to mean "serving as an example, instance, or illustration". Any embodiment or design described herein as "exemplary" is not necessarily to be construed as preferred or advantageous over other embodiments or designs.

[0009] It should be understood that the terms "on", "over", "top", "bottom", "down", "side", "back", "left", "right", "front" etc., when used in the following description are used for convenience and to aid understanding of relative positions or directions, and not intended to limit the orientation of any device or structure or any part of any device or structure.

[0010] A first layer over a second layer may include the first layer on the second layer or the first layer separated from the second layer by one or more intervening layers.

[0011] FIG. 1 is a schematic 100 showing a conductive paper according to various embodiments. The conductive paper may include a first layer 102 including an electrically conductive nanostructured material. The conductive paper may also include a second layer 104 over the first layer 102, the second layer 104 including a cellulose material. The conductive paper may further include an intermediate layer 106 between the first layer 102 and the second layer 104, the intermediate layer 106 including the electrically conductive nanostructured material interspersed between the cellulose material.

[0012] In other words, a paper including cellulose material and electrically conductive nanostructured material may be provided. The cellulose material may be on the electrically conductive nanostructured material so that the paper includes a first layer having the electrically conductive nanostructured material, a second layer having the cellulose material as well as an intermediate layer between the first layer and the second layer, the intermediate layer containing electrically conductive nanostructured material interspersed or interfused with the cellulose material. Various embodiments may provide a flexible conducting medium for various applications. Various embodiments may provide a medium which is transparent or have a high degree of transparency. Various embodiments may provide a medium with high tensile strength.

[0013] In various embodiments, the intermediate layer may also be referred to as an interfacial region or an interfuse layer. The intermediate layer may be a very thin layer. The intermediate layer may have a thickness greater than zero nm. The intermediate layer may be an intermix layer including the cellulose material and the electrically conductive nanostructured material. The first layer may be a separate, distinct layer from the second layer. If the transferred layer includes densely packed materials such as graphene or MoS_2 , the intermediate layer may be typically a very thin interfused layer.

[0014] In various embodiments, the cellulose material may be or may include a plurality of cellulose nanofibrils (CNFs). A nanofibril may be a fine fiber or filament

with a diameter in the nanometer range. The cellulose nanofibrils may also be referred to as a nanocellulose material. Each cellulose nanofibril of the plurality of cellulose nanofibrils may have a width or diameter of less than about 100 nm, or less than about 50 nm, or less than about 40 nm, or less than about 30 nm, e.g. of about 20 nm. A cellulose nanofibril may further have a length in the micrometer range.

[0015] In contrast, conventional paper may be made of cellulose fibers with diameters in the micrometer range, e.g. about 20 μm . As the fiber diameter is larger than the wavelength of visible light, there is strong light scattering on the fibers as well as in the internal pores. As such, conventional paper may not be transparent.

[0016] The plurality of cellulose nanofibrils may be isolated cellulose nanofibrils. In other words, the cellulose nanofibrils may not be attached or anchored to a cellulose fiber backbone. Cellulose fibers are typically made of cellulose fibers backbones (of about 20 μm) including bundles of nanofibers or nanofibrils. The isolated cellulose nanofibrils may be standalone nanofibrils. The nanofibrils may be disintegrated from cellulose fibers by a physical liberation method in a refining system. For instance, the cellulose fibers with attached nanofibrils may be disintegrated using a high pressure homogenizer and filtered to obtain cellulose nanofibrils.

[0017] The cellulose nanofibrils may be more chemical resistant and may not melt in solvents such as acetone compared to cellulose material such as cellulose ester (a derivative of cellulose with the hydroxyl groups replaced by alkoxy groups). The cellulose ester may not be in nanoscale and may not have a high degree of transparency.

[0018] The plurality of cellulose nanofibrils may form an interconnected network of cellulose extending from the second layer 104 to the intermediate layer 106. In other words, the plurality of cellulose nanofibrils may interlock or contact or bond to one another to form the network. Bonding may include hydrogen bonding.

[0019] The electrically conductive nanostructured material may include a plurality of nanostructures. The maximal dimension of the nanostructures may be between about

0.5 nm to about 20 nm, or about 0.5 nm to about 15 nm or about 0.5 nm to about 12 nm or about 0.5 nm to about 5 nm, or about 5 nm to about 12 nm or about 5 nm to about 15 nm. The nanostructures may form an interconnected network extending from the first layer 102 to the intermediate layer 106. The nanostructures may also interlock or contact or bond to one another to form the network.

[0020] In various embodiments, as the plurality of cellulose nanofibrils form an interconnected network of cellulose extending from the second layer 104 to the intermediate layer 106 and as the nanostructures form an interconnected network extending from the first layer 102 to the intermediate layer 106 to interperse with the cellulose nanofibrils at the intermediate layer 106, an integrated conductive paper may be formed. The integrated conductive paper may possess high structural strength.

[0021] When the electrically conductive nanostructured material is interspersed between or interfused with the cellulose material, the surface area of interaction between the electrically conductive nanostructured material and the cellulose material may be increased, giving rise to enhanced interaction between the electrically conductive nanostructured material and the cellulose material. The interaction may include physical interaction such as interlocking or entanglement (e.g. between nanowires and cellulose nanofibrils). The interaction may additionally or alternatively include strong van der waal attraction between the electrically conductive nanostructured material and the cellulose material. Additionally or alternatively, the electrically conductive nanostructured material may be attached to the cellulose material directly through functional groups such as hydroxyl groups on the nanocellulose or present on the nanostructured material itself.

[0022] The electrically conductive nanostructured material may be or may include semiconducting nanostructured material. In other words, the term “electrically conductive nanostructured material” as used herein may include also semiconducting nanostructured material. The semiconducting nanostructured material may or may not be extrinsically doped with dopants.

[0023] The percentage composition or proportion of cellulose material may increase from interfuse layer 106 to the second layer 104. The percentage composition or proportion of electrically conductive material may increase from the interfuse layer 106 to the first layer 102. In various embodiments, the first layer 102 may be without or may be substantially devoid of the cellulose material. The first layer 102 may include less than less than 1 wt % of the cellulose material. In various embodiments, the second layer 104 may be without or may be substantially devoid of the electrically conductive nanostructured material. The second layer 104 may include less than 1 wt % of the electrically conductive nanostructured material. In various embodiments, the ratio of the electrically conductive nanostructured material to the cellulose material in the interfacial region or intermediate layer may range from 1:9 to 9:1. In various embodiments, the intermediate layer 106 may be substantially thinner than the first layer 102 and the second layer 104. The thickness of the intermediate layer 106 may be ranging from more than zero to about the diameter of the electrically conductive nanostructured material (e.g. Ag nanowires) used. When the electrically conductive material includes densely packed graphene or MoS₂ layer, the intermediate layer may be an interfused layer of very small thickness.

[0024] The nanostructures may include one or more of a group consisting of nanoparticles, nanotubes, nanowires, nanosheets. The nanostructures may be or may include metallic nanowires or semiconductor nanowires. The nanostructures may be or may include nanotubes such as carbon nanotubes. The nanostructures may be or may include nanosheets such as graphene sheets or graphene oxide sheets. The nanostructures may include molybdenum disulphide (MoS₂) or tungsten disulphide (WS₂) nanostructures.

[0025] In various embodiments, the conductive paper may include a light scattering reduction material. The first layer 102, the second layer 104 and/or the intermediate layer 106 may include the light scattering reduction material. The light scattering reduction material may be a polymeric material such as polydimethylsiloxane (PDMS)

or poly(methyl methacrylate) (PMMA). Other examples of light scattering reduction materials may include polymer-silica composites such as PDMS-silica composites or various resins such as acrylic resin or epoxy resin or fluoropolymer resin etc. The light scattering reduction material may further improve transparency of the conductive nanopaper. In various embodiments, a conductive paper may be formed by a method described herein.

[0026] In various embodiments, a device such as an electrochromic paper or a photodetector, the device including a conductive nanopaper, may be provided.

[0027] In various embodiments, an electrochromic paper may be provided. The electrochromic paper may include a conductive nanopaper. The electrochromic paper may also include an electrochromic material on the conductive nanopaper. The electrochromic material may be or may include tungsten oxide (WO_3). Besides WO_3 , other suitable electrochromic materials may be or may include other transitional metal oxides such as nickel oxide (NiO) cobalt oxide (Co_3O_4) and vanadium oxide (V_2O_5), conducting polymers such as functionalized polypyrroles, polythiophenes and polyanilines as well as molecular dyes such as Ethyl Viologen (EV), Prussian blue, Pedot etc.

[0028] The electrochromic material may be or may include a plurality of electrochromic nanostructures such as WO_3 nanoparticles or NiO nanowires attached or anchored to the conductive nanopaper. In various embodiments, an electrochromic paper may be formed by a method described herein.

[0029] In various embodiments, a photodetector may be provided. The photodetector may include a conductive nanopaper. The electrically conductive nanostructured material may be a photosensitive conducting (or semiconducting) material such as MoS_2 . The photodetector may further include a first electrode in contact with a first side or portion of the first layer (including the electrically conductive nanostructured material) and a second electrode in contact with a second side or portion of the first layer.

[0030] The conductive paper may include a first layer 102 including an electrically conductive nanostructured material. The conductive paper may also include a second layer 104 over or under the first layer 102, the second layer 104 including a cellulose material. The conductive paper may further include an intermediate layer 106 between the first layer 102 and the second layer 104, the intermediate layer including the electrically conductive nanostructured material interspersed between the cellulose material. The first layer 102, the second layer 104 and the intermediate layer 106 may further include a light scattering reduction material.

[0031] FIG. 2 is a schematic 200 illustrating a method to form a conductive nanopaper according to various embodiments. The method may include, in 202, forming a first layer over a membrane, the first layer including an electrically conductive nanostructured material. The method may also include, in 204, forming a second layer, the second layer including cellulose material, over the first layer so that an intermediate layer including the electrically conductive nanostructured material and the cellulose material is formed between the first layer and the second layer by interspersing of the electrically conductive nanostructured material between the cellulose material, thereby forming a stacked structure including the first layer, the second layer and the intermediate layer. The method may further include, in 206, separating the stacked structure from the membrane to form the conductive paper.

[0032] In other words, a conductive nanopaper may be formed by introducing electrically conductive nanostructured material over a membrane, followed by introducing cellulose material on the electrically conductive nanostructured material,. A stacked structure may result. The stacked structure may include a first layer including the electrically conductive nanostructured material, a second layer including the cellulose material and an intermediate layer between the first layer and the second layer, the intermediate layer including the electrically conductive nanostructured material interspersed between or interfused with the cellulose material.

[0033] In various alternate embodiments, the method may include forming a second layer over the membrane, the second layer including the cellulose material. The method may also include forming a first layer over the second layer, the first layer including the electrically conductive nanostructured material so that an intermediate layer including the electrically conductive nanostructured material and the cellulose material is formed between the first layer and the second layer by interspersing of the electrically conductive nanostructured material between the cellulose material, thereby forming a stacked structure including the first layer, the second layer and the intermediate layer. The method may further include separating the stacked structure from the membrane to form the conductive paper.

[0034] However, forming the first layer on the membrane first may have significant advantages over forming the second layer on the membrane first. Forming the second layer including the cellulose material first may result in a rough surface. This may result in poor interconnection between the electrically conductive nanostructured material subsequently introduced on the cellulose material. Conversely, forming the first layer including the electrically conductive nanostructured material first may ensure that the electrically conductive nanostructured material are interconnected to one another and to the cellulose material. As a result, the conductive nanopaper fabricated by forming the first layer first, followed by the second layer over the first layer, may have better conductivity.

[0035] The membrane may be a porous membrane such as a polycarbonate membrane or a cellulose membrane. References to a membrane may include references to any suitable apparatus which is able to separate out the nanocellulose from a mixture as well as to separate out electrically conductive nanostructured material from a mixture.

[0036] Forming the first layer may include filtering a mixture including the electrically conductive nanostructured material through the membrane so that the electrically conductive nanostructured material is deposited over or on the membrane. The mixture may include the electrically conductive nanostructured material

suspended in or mixed with a suitable medium, such as water. When the mixture of the electrically conductive nanostructured material and the suitable medium is introduced to the membrane, the suitable medium may be substantially drained from the membrane, e.g. through pores on the membrane, leaving the electrically conductive nanostructured material on the membrane.

[0037] Filtering the mixture including the electrically conductive nanostructured material through the membrane may include introducing a plurality of droplets of the mixture including the electrically conductive nanostructured material to or over the membrane. The plurality of droplets may be introduced to the membrane using a pipette or a micro-pipette array dispenser. The mixture of electrically conductive nanostructured material and the suitable medium may be picked up by the pipette or the micro-pipette array dispenser and may be introduced to the membrane droplet by droplet.

[0038] Introducing the plurality of droplets to the membrane may include depositing a first group of the droplets on or over the membrane so that the first group of droplets forms a first sub-layer of droplets on or over the membrane. Introducing the plurality of droplets to the membrane may further include depositing a second group of the droplets on the first sub-layer of droplets so that the second group of droplets forms a second sub-layer of droplets on the first sub-layer of droplets. The droplets may have a good adhesion and may substantially maintain their shapes to form the sub-layers.

[0039] Subsequently, the method may include depositing a third group of the droplets on the second sub-layer of droplets so that the third group of droplets forms a third sub-layer of droplets on the second sub-layer of droplets. The method may further include depositing a fourth group of the droplets on the third sub-layer of droplets so that the fourth group of droplets forms a fourth sub-layer of droplets on the third sub-layer of droplets. One or more sub-layers of droplets may be deposited to form the first layer including the electrically conductive nanostructured material.

[0040] Forming the second layer may include filtering a mixture including the cellulose material through the membrane after the first layer is formed so that the second layer is formed over the first layer. The mixture may include the cellulose material suspended in or mixed with a suitable medium, such as water. When the mixture of the cellulose material and the suitable medium is introduced, the suitable medium may be substantially drained through the electrically conductive nanostructured material and the membrane, leaving the electrically conductive nanostructured material on the electrically conductive nanostructured material.

[0041] Alternatively, the second layer may first be formed by filtering a mixture including the cellulose material through the membrane so that the cellulose material is deposited over the membrane. The first layer may be formed by filtering a mixture including the conductive nanostructured material through the membrane so that the first layer is formed over the second layer. The plurality of droplets including the conductive nanostructured material may be introduced on the cellulose material. The first group of droplets may be deposited on the cellulose material so that the first group of droplets forms a first sub-layer of droplets on the cellulose material. The second group of droplets may be deposited so that the second group of droplets forms a second sub-layer of droplets on the first sub-layer of droplets.

[0042] A stacked structure may be formed by filtering a mixture including conductive nanostructured material through a membrane and filtering a mixture including the cellulose material through the same membrane. The sequence of filtering may determine whether the second layer is formed over the first layer or the first layer is formed over the second layer.

[0043] Forming the first layer and the second layer via filtration may offer significant advantages compared to methods such as coating or printing. In coating or printing, a dry nanopaper may be coated or printed with the electrically conductive nanostructured material. The interconnection and uniformity of the conductive inks may not be guaranteed. In contrast, during filtering, uniformly deposited conductive

nanostructure network may be formed first before it can be redistributed onto the nanopaper polar surface due to van der waal force attraction. Additionally or alternatively, interpersions may lead to greater mechanical interaction such as interlocking between the cellulose material and the electrically conductive nanostructured material.

[0044] Filtration may also provide advantages to methods such as blending, doping or coating in which the entire paper may be blended, doped or coated with electrically conductive nanostructured material. For such methods, the resulting structure formed may not have distinct separate layers which are interfused at the intermediate layer or interfacial region. A greater amount of electrically conductive nanostructured material may be required, leading to waste. Further, the conductive paper formed this way may not have good conductivity as the cellulose material may interfere with the movement of electrons. A continuous conduction path may not be formed or a long winding conduction path may be formed passing through the cellulose matrix. A non-transparent conductive filler may be required to be incorporated into the cellulose matrix for nanopapers formed by methods such as blending, doping or coating. In contrast, the conductive paper formed by filtration may include a continuous conductive layer with a direct conduction path, leading to improved conductivity. Further, the conductive fillers covering the cellulose may reduce the hydrogen interaction between cellulose fibers in the matrix, thus decreasing the structural strength. For instance, Ppy-Nanocellulose composite may be brittle. In contrast, for the conductive paper formed by filtration, the hydrogen bonding in the second layer between the cellulose material may not be deteriorated and a continuous conduction formed may be formed in the first layer. The resulting conductive nanopaper may bend and even fold while still retaining the conductivity.

[0045] The method may also include disintegrating a cellulose source material to form the mixture comprising the cellulose material. The cellulose source material may be or may include natural cellulose. The cellulose material may be or may include a

plurality of cellulose nanofibrils. The plurality of cellulose nanofibrils may be or may include isolated cellulose nanofibrils.

[0046] Natural cellulose (e.g. wood pulp) may include cellulose fibers with cellulose nanofibrils aggregated in micron-bundles. The natural cellulose may be disintegrated to separate the cellulose nanofibrils from the cellulose bundles. A cellulose nanofibril may have a width or diameter in the nanometer range while a cellulose fiber may have a width or diameter in the micrometer range. Mechanical disintegration may be achieved using a homogenizer (using inline dispersing) and/or microfluidizer (using high pressure dispersing). Additionally or alternatively, disintegration may be achieved using chemical modification.

[0047] Each cellulose nanofibril of the plurality of cellulose nanofibrils may have a width or diameter of less than about 100 nm, or less than about 50 nm, or less than 40nm, or less than 30 nm, or of about 20 nm.

[0048] The method may include applying a pressure on the stacked structure before separating the stacked structure from the membrane. The pressure may be applied by arranging the stacked structure between a first clamping structure and a second clamping structure and applying a compressive force to the stacked structure via the first clamping structure and the second clamping structure. In other words, the method may involve sandwiching the stacked structure between two clamping structures and pressing the two clamping structures together. The clamping structures may be glass slides.

[0049] The method may include applying heat to the stacked structure before separating the stacked structure from the membrane. The heat may be applied when the pressure is applied. In various alternate embodiments, the method may not include applying heat to the stacked structure. In general, the temperature may be kept at about 25 °C to about 120 °C. However, the stacked structure may be heated to a temperature above the boiling temperature of water (i.e. above 100 °C, e.g. 105 °C) for the stacked structure may be dried at a faster rate.

[0050] In various embodiments, separating the stacked structure from the membrane may include peeling the stacked structure from the membrane. The stacked structure may be separated or peeled off from the membrane as a whole. As the adhesion of the electrically conductive nanostructured material to the cellulose material may be greater compared to the adhesion of the electrically conductive nanostructured material to the membrane, the electrically conductive nanostructured material may be separated from the membrane together with the cellulose material as a single integrated stacked structure.

[0051] In various embodiments, the method may include adding a light scattering reduction material to the stacked structure. The light scattering reduction material may include polymethylsiloxane (PDMS). The light scattering reduction material may be added to the first layer, the second layer and/or the intermediate layer. Adding the light scattering reduction material may include applying the light scattering reduction material to the stacked structure or impregnating the stacked structure with the light scattering reduction material. Adding the light scattering reduction material to the stacked structure may further improve transparency of the conductive nanopaper and may reduce hazing.

[0052] In various embodiments, the electrically conductive nanostructured material may include one or more of a group consisting of nanoparticles, nanotubes, nanowires, nanosheets. The electrically conductive nanostructured material may include semiconducting nanostructured material.

[0053] In various embodiments, a method to form a conductive nanopaper may include forming a first layer, the first layer including an electrically conductive nanostructured material. The method may also include forming a second layer, the second layer including cellulose material, over or under the first layer so that an intermediate layer including the electrically conductive nanostructured material and the cellulose material is formed between the first layer and the second layer by interspersing of the electrically conductive nanostructured material between the

cellulose material, thereby forming a stacked structure including the first layer, the second layer and the intermediate layer, the stacked structure over a membrane. The method may further include separating the stacked structure from the membrane to form the conductive paper. The method may include adding a light scattering reduction material to the stacked structure.

[0054] A method of forming a device such as an electrochromic paper may be provided according to various embodiments. The method may include forming a conductive nanopaper. The method may include introducing electrochromic material to the conductive nanopaper. The electrochromic material may be attached or anchored to the conductive nanopaper. The electrochromic material may include a plurality of electrochromic nanostructures anchored to the conductive nanopaper. The electrochromic material may include tungsten oxide.

[0055] A method of forming a photodetector may be provided according to various embodiments. The method may include forming a conductive nanopaper. The method may further include forming a first electrode to contact a first side or portion of the first layer. The method may further include forming a second electrode to contact a second side or portion of the first layer. The electrically conductive nanostructured material may include a photosensitive conducting or semiconducting material.

[0056] FIG. 3A is a photo 300a of a transparent nanopaper according to various embodiments. The transparent nanopaper is positioned in front of a background with wordings and the wordings are clearly visible from the photo, indicating transparency of the nanopaper. As the average diameter of the cellulose nanofibrils (CNFs) is much smaller than the wavelength of visible light with greatly reduced light scattering, a nanopaper may be transparent or have a high degree of transparency.

[0057] In various embodiments, the conductive paper may be a conductive nanopaper. Nanopaper may be obtained or formed from CNFs. A nanopaper may refer to a paper including or made of CNFs. In one example, 3 wt% of CNF may be taken for 1.0 g and mixed with 100 ml DI water to form a suspension. The suspension may be stirred well

before vacuum filtration. The filtered CNF may form a “cake” on the filter membrane. The “cake” with the membrane may be arranged or sandwiched between two flat glass slides in an oven at about 105 °C to dry up. A nanopaper may be obtained based on this refining filtration method.

[0058] FIG. 3B is a schematic 300b showing a setup to measure a transparency of a substrate according to various embodiments. A substrate 302 such as a nanopaper may be positioned between a light source 304 and an integrating sphere detector 306. The integrating sphere detector 306 may detect the amount of light from the light source 304 transmitted through the substrate 302.

[0059] FIG. 3C is a scanning electron microscopy image 300c of a nanopaper according to various embodiments. As shown in FIG. 3C, the nanopaper may include a plurality of isolated CNFs (i.e. not bundled together to form a cellulose fiber) forming an interconnected network.

[0060] FIG. 3D is a graph 300d of counts against diameter (nm) showing the diameter distribution of a sample of cellulose nanofibrils (CNFs) according to various embodiments. As shown in FIG. 3D, CNFs with diameters of about 20 nm may form the largest proportion of CNFs in a sample of CNFs. The diameters of the CNFs may range from about 15 nm to about 35 nm.

[0061] FIG. 4A is a flowchart 400a showing a method of forming a conductive nanopaper according to various embodiments. FIG. 4B is a schematic 400b illustrating the method shown in FIG. 4A according to various embodiments. The method may be referred to as a hot transfer method. In 410, a filtration system may be set up. The filtration system may include a filtration membrane 406, e.g. a polycarbonate (PC) filter membrane. In 420, a suspension or mixture of electrically conductive nanostructured material (e.g. Ag nanowires 402) may be filtered through the membrane 406 to form a continuous conductive thin film. In various embodiments, about 0.5 to about 1.0mg of Ag nanowires may be used. In 430, a suspension or mixture 408 of cellulose material (e.g. nanocellulose material 404) may also be

filtered through the same membrane 406 for filtering the Ag nanowires 402 so that the nanocellulose material 404 may be on top of the Ag nanowires 402. In 440, the stacked structure including the nanocellulose material 404 and the Ag nanowires 402 may be sandwiched between two glass slides 412a, 412b and kept at about 105 ° C in an oven to dry. The stacked structure including the nanocellulose material 404 (i.e. nanopaper) with the continuous thin transparent Ag nanowire thin film 402 may then be peeled off the membrane 406 in 450 to form a conductive nanopaper. As the adhesion of the Ag nanowires 402 to the nanopaper is greater than the adhesion of the Ag nanowires to the membrane, the Ag nanowires 402 may be transferred to the nanopaper 404 as a continuous conductive thin film or layer when the nanopaper is peeled off from the membrane 406. The abundant hydroxyl groups on nanocellulose material 404 may interact more strongly with the Ag nanowires 402 at an elevated temperature than the membrane 406 does. The conductive nanopaper may include a first layer including the Ag nanowires 402, a second layer including the nanocellulose material 404 and an intermediate layer between the first layer and the second layer, the intermediate layer including the Ag nanowires 402 interspersed between the nanocellulose material 404.

[0062] The hot transfer method may be performed in the temperature range of about 25 to about 120 °C. For practical and fast operation, the temperature may be set above 100 °C (the boiling temperature of water), e.g. about 105 °C.

[0063] In one example, an excellent conductivity with sheet resistance of about 0.77 Ω / sq may be achieved. The Ag nanowires may be replaced by other metallic nanowires, CNTs or graphene, one-dimensional conducting oxide nanowires, or two-dimensional layer semiconducting materials such as MoS₂, WS₂, etc.

[0064] The Ag nanowires may be replaced by semiconducting nanostructured material. In other words, electrically conductive nanostructured material may include semiconductor nanomaterials such as zinc oxide (ZnO). The semiconducting nanostructured material may or may not be doped with extrinsic dopants.

[0065] The electrically conductive nanostructured material may generally include metallic nanostructures (e.g. nanowires or nanoparticles) or semiconductor nanostructures (e.g. nanowires or nanoparticles) or other semi-conductive/conductive nanostructures. The electrically conductive nanostructured material may include for instance, carbon nanotubes, graphene, reduced graphene oxide, conducting polymers, metallic nanostructures, molybdenum disulphide (MoS_2) nanostructures and/or tungsten disulphide (WS_2) nanostructures.

[0066] In various embodiments, about 0.5 to about 1 g of about 3 to about 10 wt % of CNF may be used to get a nanopaper with sufficient transparency. The larger the weight, the higher the maximum breakdown stress the nanopaper may sustain.

[0067] The diameter of a CNF may be determined by the source of natural cellulose as well as the method to separate cellulose into nanoscale. CNF may be disintegrated from tree pulps by a physical liberation method. The diameter may be, for instance, in the range of about 15 nm to about 35 nm. The smaller the diameter of the CNF, the better the transparency of the nanopaper.

[0068] In other words, nanocellulose material 404 may be made via the disintegration of natural cellulose fibres into nanoscaled fibres by the physical liberation method. As highlighted previously, the nanoscale dimension of nanocellulose material 404 may allow the fabricated nanopaper to be transparent or have a high degree of transparency. Also, due to the reduction in fibril size, the mechanical strength of fabricated conductive nanopaper may be greatly enhanced.

[0069] In addition, the Ag nanowires 402 (or any conducting nanomaterial) and the nanocellulose material 404 may be integrated through van der Waals or chemical bonding. The relocation of Ag nanowires may be attained via the hot transfer method to form the conductive nanopaper. Additionally, by using the hot transfer method, the continuity of the Ag nanowires 402 (or any conducting nanomaterial) may be greatly improved compared to other methods such as coating or printing processes, which may lead to improvement in conductivity.

[0070] The hot transfer method may allow the electrically conductive nanostructured material (e.g. Ag nanowires 402) to be interspersed with the cellulose material (e.g. nanocellulose material 404). An intermediate layer or interfacial region between a first layer including the electrically conductive nanostructured material 402 and a second layer including the cellulose material 404 may be formed, the intermediate layer or interfacial region including the electrically conductive nanostructured material 402 interfused with the cellulose material 404.

[0071] Superior mechanical properties arise from the reduced fiber size and thus an increased density and stronger interactions between fibers. . FIG. 5A shows a graph 500a of stress (MPa) against strain (%) of a conductive nanopaper formed according to various embodiments. The tensile strength of the conductive nanopaper may reach about 20 GPa as shown in FIG. 5A.

[0072] When the suspension or mixture 408 of nanocellulose material 404 is added to the continuous thin transparent Ag nanowire thin film 402 on the membrane, the Ag nanowires 402 may come between the nanocellulose material 404 to form the intermediate layer or interfacial region. The interspersed of the electrically conductive nanostructured material between the cellulose material may provide a large surface area between the electrically conductive nanostructured material and the cellulose material, thus increasing the intensity of interaction between the electrically conductive nanostructured material and the cellulose material (e.g. between the hydroxyl groups of the cellulose material and hydroxyl groups bound to the surface of the electrically conductive nanostructured material or van der waal forces between the cellulose material and the electrically conductive nanostructured material) when the stacked structure is dried or heated, leading to an integrated nanopaper. The interspersed of the electrically conductive nanostructured material between the cellulose material may also increase the amount of mechanical interaction between the electrically conductive nanostructured material and the cellulose material.

[0073] The great tensile strength may also arise from the nanopaper with enhanced density and thus enhanced hydrogen bonding interaction between fibers.

[0074] Compared to methods such as roll coating, spraying, blending or doping, the hot transfer method may enable full utilization of the electrically conductive nanostructured material and only a very small amount of electrically conductive nanostructured material may be required to form a continuous transparent conductive layer (i.e. the first layer) on the conductive paper. Also, as the amount of electrically conductive nanostructured material added may be small, the light scattering effect caused by the electrically conductive nanostructured material may be reduced. Additionally, the use of conductive fillers (which may not be transparent) may not be required, thus further improving transparency.

[0075] FIG. 5B shows a field emission scanning electron microscopy (FESEM) image 500b of cellulose nanofibrils (CNFs) according to various embodiments. Due to fibrils size reduction, the light scattering effect may also be reduced substantially, causing the nanopaper or conductive nanopaper to be more transparent than a regular paper. When an object is less than one tenth of the light wavelength, it may be free from the scattering. As can be seen from the FESEM image 500b, the nanofibril may be micrometers long and may be about 20 nm in width.

[0076] Transparency may be determined by measuring transmittance of light in a setup such as the setup shown in FIG. 3B. FIG. 6A shows a graph 600a of transmittance (%) against wavelength (nm) of various samples positioned at about zero mm from an integrating sphere detector ($d = 0$ mm). 602 indicates the results for a nanopaper including CNFs, 604 indicates the results of a conductive nanopaper including CNFs and Ag nanowires, 606 indicates the results of a PDMS treated nanopaper, and 608 indicates the results of a glass slide (used as a reference). FIG. 6B shows a graph 600b of transmittance (%) against wavelength (nm) of various samples positioned at about twenty mm from an integrating sphere detector ($d = 20$ mm). 612 indicates the results for a nanopaper including CNFs, 614 indicates the results of a conductive nanopaper

including CNFs and Ag nanowires, 616 indicates the results of a PDMS treated nanopaper (without Ag nanowires), and 618 indicates the results of a glass slide (used as a reference). The light used may be in the ultraviolet – visible (uv – vis) range. FIG. 6C shows a graph 600c of transparency (%) against distance (mm) measured for light of wavelength of about 600 nm.

[0077] FIG. 7A shows a photo 700a of a nanopaper according to various embodiments held to the background. FIG. 7B shows a photo 700b of a nanopaper according to various embodiments held at a distance from the background. FIG. 7C shows a photo 700c of a nanopaper (without Ag nanowires) treated with PDMS according to various embodiments held to the background. FIG. 7D shows a photo 700d of a nanopaper treated with PDMS according to various embodiments held at a distance from the background.

[0078] As shown in FIG. 6A, the vacuum filtered nanopaper may exhibit a transparency of around 90 % in the visible range (at zero distance from an integrating sphere detector). The transmittance is impressive with the transparency almost the same as the glass slide. However, the conductive nanopaper may exhibit a hazing effect. The transparency may decrease with the increase of distance from the object. The light from the light source may be scattered to wide angles causing the source light intensity to decrease. This behaviour may be evident from FIGS. 6B, 6C and FIG. 7B, 7D.

[0079] In various embodiments, the conductive nanopaper or nanopaper may include a light scattering reduction material to further improve transparency and/or reduce hazing. The light scattering reduction material may be a polymeric material such as polydimethylsiloxane (PDMS). PDMS resin impregnation may cause the surface of the nanopaper or conductive nanopaper to be flattened. Consequently, light scattering may be reduced, which leads to a higher transparency. The transmittance loss with distance for PDMS treated nanopaper may be slower than pristine nanopaper as shown in FIG. 6C, indicating reduced hazing effect. Impregnation of other resin or polymer matrix with reduced refractive index may also be employed.

[0080] In various embodiments, the conductive nanopaper may have about 5% to about 100% transmission, e.g. about 20% to about 70% transmission, e.g. about 40% to about 60% transmission in the visible and/or ultraviolet range. For instance, a conductive nanopaper of about 50% transmission in the visible range with Ag nanowires. Transparency of the conductive nanopaper may further be improved by addition of one or more light scattering reduction material as described herein or by adjusting the amount of electrically conductive nanostructured material used.

[0081] As mentioned previously, another good advantage of the hot transfer method is that the electrically conductive nanostructured material on the membrane may be transferred or relocated to nanopaper in a continuous intact way. As a result, the surface of nanopaper may be conductive with a very low sheet resistance. Various embodiments may include filtering a mixture including the electrically conductive nanostructured material through a membrane so that the electrically conductive nanostructured material is deposited on the membrane (to form the first layer) and filtering a mixture including the cellulose material through the membrane (to form the second layer) after the first layer is deposited so that the second layer is formed over the first layer. An intermediate layer including the cellulose material and the electrically conductive nanostructured material may also be formed between the first layer and the second layer. Various alternate embodiments may include filtering a mixture including the cellulose material through the membrane so that the cellulose material is deposited on the membrane (to form the second layer) and filtering a mixture including the electrically conductive nanostructured material (to form the first layer) after the second layer is deposited so that the first layer is formed over the second layer. However, if the filtering of electrically conductive nanostructured material such as Ag nanowires is performed onto a rough nanopaper surface after the nanopaper is made, it may not be as conductive. Surface roughness may play a critical role in ensuring good conductivity. If the second layer including the cellulose material is formed first, the rough surface of the second layer may result in poor interconnection

between the electrically conductive nanostructured material (e.g. Ag nanowires) subsequently deposited on the cellulose material. On the other hand, forming the first layer including the electrically conductive nanostructured material first (followed by forming the second layer including cellulose material) may ensure that the electrically conductive nanostructured material (e.g. Ag nanowires) are interconnected to one another first. Forming the first layer, followed by the second layer over the first layer may lessen the dependence and sensitivity of electrical conductivity on surface roughness.

[0082] FIG. 8A is a photo 800a showing the resistance measurement of a conductive nanopaper formed by a method including depositing electrically conductive nanostructured material first, followed by depositing the cellulose material on the electrically conductive nanostructured material according to various embodiments. FIG. 8B is a photo 800b showing showing the resistance measurement of a conductive nanopaper formed by a method including depositing the cellulose material first, followed by depositing the electrically conductive nanostructured material on the cellulose material according to various embodiments. The reading of the conductive paper in FIG. 8A shows 3.9 ohms while the reading of the conductive paper in FIG. 8B shows 71.9 kohms. This shows that depositing electrically conductive nanostructured material first, followed by depositing the cellulose material on the electrically conductive nanostructured material may result in improved conductivity.

[0083] A selective layering approach may be used to improve conductivity of the flexible, conductive nanopaper. The filtering of the mixture including the electrically conductive nanostructured material through the membrane may be carried out by introducing the electrically conductive nanostructured material to the membrane in a plurality of droplets of the mixture including the electrically conductive nanostructured material. FIG. 9A is a schematic 900a illustrating introduction of a plurality of droplets 902 including the electrically conductive nanostructured material to the membrane 906 according to various embodiments. The plurality of droplets 902

may be introduced to the membrane 906 using a pipette or a precision manifold micro-pipette array dispenser. 100 μ L of 0.25 mg/mL of multiple droplets of AgNW droplet may be introduced to the membrane 906 and subsequently transferred to the nanocellulose material.

[0084] FIG. 9B is a schematic 900b further illustrating the selective layering approach according to various embodiments. Any number of droplets may be introduced to the membrane. In 910, 9 droplets 902 may be introduced to the membrane. In 920, 13 droplets 902 may be introduced. 9 droplets 902 may be deposited on the membrane 906, followed by another 4 droplets 902. In 930, 19 droplets may be introduced. 9 droplets 902 may be deposited on the membrane 906, followed by another 4 droplets 902, followed by another 6 droplets. In 940, 28 droplets may be introduced. 9 droplets 902 may be deposited on the membrane 906, followed by another 4 droplets 902, followed by another 6 droplets, followed by 9 droplets.

[0085] FIGS. 10A – 10D illustrate the sequential deposition of droplets according to various embodiments. FIG. 10A is a schematic 1000a showing a first group of droplets 1002a being deposited according to various embodiments. The membrane is not shown in FIGS. 10A – 10D. The method may include depositing a first group of the droplets 1002a on the membrane so that the first group of droplets 1002a forms a first sub-layer of droplets 1002a on the membrane. FIG. 10B is a schematic 1000b showing a second group of droplets 1002b being deposited according to various embodiments. The method may further include depositing a second group of the droplets 1002b on the first sub-layer of droplets 1002a so that the second group of droplets 1002b forms a second sub-layer of droplets 1002b on the first sub-layer of droplets 1002a. FIG. 10C is a schematic 1000c shows a third group of droplets 1002c being deposited according to various embodiments. The method may further include depositing a third group of the droplets 1002c on the second sub-layer of droplets 1002b so that the third group of droplets 1002c forms a third sub-layer of droplets 1002c on the second sub-layer of droplets 1002b. The second sub-layer 1002b is

hidden from view in FIG. 10C. FIG. 10D is a schematic 1000d showing a fourth group of droplets 1002d being deposited according to various embodiments. The method may further include depositing a fourth group of the droplets 1002d on the third sub-layer of droplets 1002c so that the fourth group of droplets 1002d forms a fourth sub-layer of droplets 1002d on the third sub-layer of droplets 1002c.

[0086] The plurality of droplets may be viewed as 4 different sub-layers 1002a, 1002b, 1002c, 1002d which may be deposited consecutively. In one instance, the first sub-layer 1002a may spread 9 droplets of Ag nanowires across a 40mm diameter circular membrane, follow by second sub-layer 1002b and third sub-layer 1002c for connecting the droplets in the first sub-layer 1002a. Lastly, the 4th sub-layer 1002d may reinforce the first sub-layer of droplets 1002a for enhancement of conductivity.

[0087] FIG. 11 is a box plot 1100 of sheet resistance (ohms/square) of multiple point measurements on a conductive nanopaper formed with the selective layering approach according to various embodiments. The conductive nanopaper may include 28 droplets of Ag nanowires on nanocellulose material. The box in FIG. 11 indicates the sheet resistance of each of the droplets. FIG. 11 shows the controllability of sheet resistance with varying amount of nanowires. The average sheet resistance is about 3.59 ohms/square with the data ranging from about 3.3 to about 3.8 ohms/square.

[0088] To achieve an average sheet resistance of 3.59 ohms/square, 28 droplets of 100 μ L AgNW with 0.25mg/mL concentration may be vacuum filtrated. The volume of droplets may be controlled by micropipettes. Specific amount of metallic Ag nanowires may be transferred using a precision manifold micropipette array dispenser to rationally tailor the spatial distribution of nanowires. The low amount of nanowires used in the selective layering approach may help reduce costs. The transmittance of a conductive paper including Ag nanowires/nanocellulose (28 droplets configuration) may be about 78.99T% at 600 nm wavelength.

[0089] FIGS. 12A – F illustrate a method to form a conductive nanopaper using the selective layering approach according to various embodiments. FIG. 12A is a

schematic 1200a showing a membrane 1206 being provided according to various embodiments. The membrane 1206 may be a polycarbonate filter membrane. FIG. 12B is a schematic 1200b showing a plurality of droplets 1202 being deposited on or introduced to the membrane 1206 according to various embodiments. The plurality of droplets 1202 may include Ag nanowires. The Ag nanowires may be suspended in water or any other suitable medium. One or more sub-layers of droplets may be deposited on or introduced to the membrane 1206 in the selective layering approach. FIG. 12C is a schematic 1200c showing nanocellulose material 1204 being vacuum filtered on the Ag nanowire droplets 1202 according to various embodiments. FIG. 12D is a schematic 1200d showing a stacked structure including the nanocellulose material 1204 and the Ag nanowire droplets 1202 being dried according to various embodiments. The stacked structure may be pressed between two glass slides 1212a, 1212b and heated to dry the stacked structure. FIG. 12E is a schematic 1200e showing the stacked structure being peeled off from the membrane 1206 according to various embodiments. As the adhesion of the Ag nanowire droplets 1202 to the nanocellulose material 1204 is greater than the adhesion of the droplets 1202 to the membrane 1206, the Ag nanowire 1202 may be separated from the membrane 1206 together with the nanocellulose material 1204. FIG. 12F is a schematic 1200f showing a conductive nanopaper including the Ag nanowires 1202 and the nanocellulose material 1204 according to various embodiments. The conductive nanopaper may include a first layer including the Ag nanowires 1202, a second layer over the first layer including the nanocellulose material 1204 and an intermediate layer or interfacial region between the first and second layer, the intermediate layer or interfacial region including Ag nanowires 1202 interspersed with nanocellulose material 1204.

[0090] Various embodiments may provide a refining filtration method to fabricate a flexible, foldable and transparent conductive nanopaper. The nanopaper may have a high mechanical strength, e.g. about 20 GPa (Young's Modulus), with good transparency. The method may include a hot transfer method for relocating

electrically conductive nanostructured materials from a polycarbonate membrane to nanopaper for fabricating transparent, conductive nanopapers with an excellent conductivity of sheet resistance of only $0.77 \Omega / \text{sq}$. Various embodiments may involve a simple and efficient transfer method, which may lead to a lot of possibilities in fabricating novel devices.

[0091] Devices may be formed using the transparent conductive nanopaper. Preliminary results demonstrate the feasibility of nanopaper incorporated devices. Electrochromic nanopaper may be formed using the transparent conductive nanopaper. Electrochromism may refer to the phenomenon of reversibly changing color when a charge is applied. An electrochromic material may be able to reversibly change its colour when it is placed in a different electronic state. By absorbing an electron (the electrochromic material is reduced) or by ejecting one (the electrochromic material is oxidised), the material may be able to change its colour. Various types of materials and structures may be used to construct electrochromic device. Electrochromism may occur due to the electrochemical redox reactions that take place in electrochromic materials.

[0092] An electrochromic nanopaper may be made by first making a conductive transparent paper. An electrochromic material such as tungsten oxide (WO_3) may be deposited on the conductive nanopaper. The WO_3 may be electrochemically deposited for a predetermined duration of time (e.g. about 100s) onto the conductive nanopaper from peroxotungstic acid (PTA) in a three electrode environment.

[0093] FIGS. 13A and 13B show the operation of an electrochromic paper according to various embodiments. FIG. 13A is a photo 1300a of an electrochromic paper being applied with a potential difference of about +0.3 V relative to a Ag/AgCl reference electrode according to various embodiments. FIG. 13B is a photo 1300b of the electrochromic paper (shown in FIG. 13A) being applied with a potential difference of about -0.7 V relative to the Ag/AgCl reference electrode according to various embodiments. WO_3 exhibits a metallic yellowish colour at about +0.3 V and a dark blue colour at about -0.7V. As shown in FIGS. 13A, 13B, the active electrochromic

material (i.e. WO_3) biased at different potential differences (such as about + 0.3 V and about -0.7V) relative to a reference electrode (such as Ag/AgCl reference electrode in LiClO_4 , propylene carbonate electrolyte) may exhibit an obvious change in colour, making the electrochromic paper practical for real applications.

[0094] As the conductive nanopaper surface covered with hydrophilic OH functional groups bound to the CNFs, the nanofibrils may serve as a reservoir for PTA storage and/or an easy anchoring surface for deposited WO_3 . This may lead to full coverage of WO_3 nanoparticles over the conductive nanopaper surface in a short time.

[0095] FIG. 14A is a field emission scanning electron microscopy (FESEM) image 1400a of a conductive nanopaper according to various embodiments. FIG. 14B is a field emission scanning electron microscopy (FESEM) image 1400b of an electrochromic paper including tungsten oxide on the conductive nanopaper according to various embodiments. FIG. 14C is a magnified field emission scanning electron microscopy (FESEM) image 1400c showing tungsten oxide (WO_3) nanoparticles anchored to a cellulose nanofibril according to various embodiments. The enhanced electrochemical performance of conductive nanopaper may lead to an electrochromic paper more densely covered with WO_3 , which may contribute to the high color contrast. Besides WO_3 , other suitable electrochromic materials may include other transitional metal oxides such as nickel oxide (NiO) and cobalt oxide (CoO), conducting polymers such as functionalized polypyrroles, polythiophenes and polyanilines as well as molecular dyes such as Ethyl Viologen (EV).

[0096] The transfer method may be used in other device applications like photodetectors and transistors. This advanced platform technology of producing conductive nanopapers may be scalable and competitive from a market and manufacturing prospective.

[0097] FIGS. 15A-D illustrate a method of forming a photodetector according to various embodiments. FIG. 15A is a schematic 1500a showing forming a first layer 1502 on a membrane 1506 according to various embodiments. The first layer 1502 may

include an electrically conductive nanostructured material such as molybdenum disulphide (MoS_2) nanostructures, e.g. MoS_2 nanosheets. Before forming the first layer 1502, a suitable masking material such as PDMS may be deposited on the membrane 1506 and patterned to form a masking layer 1514. Patterning may involve a lithographic method such as photolithography. The electrically conductive nanostructured material may then be deposited, e.g. using filtration, on the membrane to form the first layer 1502.

[0098] FIG. 15B is a schematic 1500b showing forming a second layer 1504 over the first layer 1502 according to various embodiments. The second layer 1504 may include a cellulose material such as a nanocellulose material. The masking layer 1514 may be removed prior to forming the second layer 1504. The cellulose material may be deposited on the electrically conductive nanostructured material using a suitable method such as filtration. An intermediate layer (not shown) including the electrically conductive nanostructured material and the cellulose material may be formed between the first layer 1502 and a portion of the second layer 1504 by interspersing of the electrically conductive nanostructured material between the cellulose material.

[0099] FIG. 15C is a schematic 1500c showing the stacked structure being separated from the membrane 1506 according to various embodiments. The stacked structure may be peeled off from the membrane 1506. The stacked structure may be reoriented so that the first layer 1502 may be over the second layer 1504. FIG. 15D is a schematic 1500d showing electrodes 1518a, 1518b on the stacked structure according to various embodiments. A first electrode 1518a may be formed on a first end region of the stacked structure and electrically contacting the first layer 1502. A second electrode 1518b may be formed on a second end region of the stacked structure and electrically contacting the first layer 1502. The first electrode 1518a may be separated or isolated from the second electrode 1518b. In other words, there may be a gap between the first electrode 1518a and the second electrode 1518b, the gap exposing the first layer 1502.

The electrodes 1518a, 1518b may include a suitable conductive material such as platinum.

[00100] FIG. 16A is a schematic 1600a showing a photodetector according to various embodiments. The photodetector may include a conductive nanopaper. The conductive nanopaper may include a second layer 1604 including cellulose material. The conductive nanopaper may further include a first layer 1602 over a portion of the second layer 1604. The first layer 1602 may include an electrically conductive nanostructured material such as MoS₂ nanosheets. The conductive nanopaper may further include an intermediate layer (not shown) between the first layer 1602 and the second layer 1604. The intermediate layer may include the electrically conductive nanostructured material interspersed between the cellulose material. The photodetector may further include a first electrode 1618a on the second layer 1604 contacting a first side or portion of the first layer 1602 and a second electrode 1618b on the second layer 1604 contacting a second side or portion of the first layer 1602. The photodetector may be a transparent photodetector. FIG. 16B is a photo 1600b showing the photodetector illustrated in FIG. 16A being held at a distance from a background. There is some amount of hazing when the photodetector is held at a distance as shown in FIG. 16B and the words in the background are not clearly visible. FIG. 16C is a photo 1600c showing the photodetector shown in FIG. 16B on the background. In other words, there is zero distance between the photodetector and the background. When the photodetector is on the background, the wordings are clearly visible.

[00101] FIG. 16D is a field emission scanning electrode microscopy image (FESEM) 1600d of the disulphide (MoS₂) nanosheets according to various embodiments. FIG. 16E is a magnified field emission scanning electrode microscopy image (FESEM) 1600e of the disulphide (MoS₂) nanosheets according to various embodiments. FIG. 16F is a further magnified field emission scanning electrode microscopy image (FESEM) 1600f of the disulphide (MoS₂) nanosheets according to various embodiments.

[00102] The photodetector has also been demonstrated to work. FIGS. 17A – C illustrate the performance of the photodetector according to various embodiments. FIG. 17A is a graph 1700a of current (nA) as a function of voltage (V) measured under light condition and under dark condition according to various embodiments. 1702 shows the data under light condition while 1704 shows the data under dark condition. The photodetector exhibits a higher current under light condition compared to under dark condition. FIG. 17B is a graph 1700b of current (nA) as a function of time (s) according to various embodiments. The current may be measured while the photodetector is turned “on” (under light condition) and “off” (under dark condition). The current flowing through the detector when the photodetector is turned “on” may be about 5.65 nA and the current flowing through the detector when the photodetector is turned “off” may be about 5.4 nA. FIG. 17C is a graph 1700c of normalized current (in arbitrary units or a.u.) as a function of time (s) for set and reset operations according to various embodiments. Lines 1706 and 1708 are fitted to data measured. 1706 shows the normalized current measured during a reset operation while 1708 shows the normalized current measured during a set operation.

[00103] Methods described herein may further contain analogous features of any structure or conductive paper described herein. Correspondingly, structures or conductive papers described herein may further contain analogous features of any methods described herein.

[00104] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A method of forming a conductive paper, the method including:
 - forming a first layer over a membrane, the first layer comprising an electrically conductive nanostructured material;
 - forming a second layer, the second layer comprising cellulose material, over the first layer so that an intermediate layer comprising the electrically conductive nanostructured material and the cellulose material is formed between the first layer and the second layer by interspersing of the electrically conductive nanostructured material between the cellulose material, thereby forming a stacked structure comprising the first layer, the second layer and the intermediate layer; and
 - separating the stacked structure from the membrane to form the conductive paper.
2. The method according to claim 1,
 - wherein forming the first layer comprises filtering a mixture comprising the electrically conductive nanostructured material through the membrane so that the electrically conductive nanostructured material is deposited on the membrane.
3. The method according to claim 2,
 - wherein filtering the mixture comprising the electrically conductive nanostructured material through the membrane comprises introducing a plurality of droplets of the mixture comprising the electrically conductive nanostructured material to the membrane.

4. The method according to claim 3,
wherein introducing the plurality of droplets to the membrane comprises:
depositing a first group of the droplets on the membrane so that the first group of droplets forms a first sub-layer of droplets on the membrane; and
depositing a second group of the droplets on the first sub-layer of droplets so that the second group of droplets forms a second sub-layer of droplets on the first sub-layer of droplets.
5. The method according to claim 3 or claim 4,
wherein the plurality of droplets is introduced to the membrane using a pipette or a micro-pipette array dispenser.
6. The method according to any of claims 2 to 5,
wherein forming the second layer comprises filtering a mixture comprising the cellulose material through the membrane after the first layer is formed so that the second layer is formed over the first layer.
7. The method according to claim 6, further comprising:
disintegrating a cellulose source material to form the mixture comprising the cellulose material.
8. The method according to claim 7,
wherein the cellulose source material is natural cellulose.
9. The method according to any of claims 1 to 8,
wherein the cellulose material comprises a plurality of cellulose nanofibrils.
10. The method according to claim 9,

wherein the plurality of cellulose nanofibrils are isolated cellulose nanofibrils.

11. The method according to claim 9 or claim 10,
wherein each cellulose nanofibril of the plurality of cellulose nanofibrils has a diameter of less than 50 nm.
12. The method according to any of claims 1 to 11, further comprising:
applying a pressure on the stacked structure before separating the stacked structure from the membrane.
13. The method according to claim 12,
wherein the pressure is applied by arranging the stacked structure between a first clamping structure and a second clamping structure and applying a compressive force to the stacked structure via the first clamping structure and the second clamping structure.
14. The method according to any of claims 1 to 13, further comprising:
applying heat to the stacked structure before separating the stacked structure from the membrane.
15. The method according to any of claims 1 to 14,
wherein the stacked structure is heated to a temperature above 100 °C.
16. The method according to any of claims 1 to 15,
wherein separating the stacked structure from the membrane comprises peeling the stacked structure from the membrane.

17. The method according to any of claims 1 to 16,
wherein the membrane is a polycarbonate membrane.
18. The method according to any of claims 1 to 17, further comprising:
adding a light scattering reduction material to the stacked structure.
19. The method according to claim 18,
wherein the light scattering reduction material is polymethylsiloxane.
20. The method according to any of claims 1 to 19,
wherein the electrically conductive nanostructured material comprises one or more of a group consisting of nanoparticles, nanotubes, nanowires, nanosheets.
21. The method according to any of claims 1 to 20,
wherein the electrically conductive nanostructured material comprises semiconducting nanostructured material.
22. A conductive paper formed by a method according to any of claims 1 to 21.
23. A conductive paper comprising:
a first layer comprising an electrically conductive nanostructured material;
a second layer over the first layer, the second layer comprising a cellulose material; and
an intermediate layer between the first layer and the second layer, the intermediate layer comprising the electrically conductive nanostructured material interspersed between the cellulose material.

24. The conductive paper according to claim 23,
wherein the cellulose material comprises a plurality of cellulose nanofibrils.
25. The conductive paper according to claim 24,
wherein the plurality of cellulose nanofibrils are isolated cellulose nanofibrils.
26. The conductive paper according to claim 24 or claim 25,
wherein each cellulose nanofibril of the plurality of cellulose nanofibrils has a diameter of less than 50 nm.
27. The conductive paper according to any of claims 24 to 26,
wherein the plurality of cellulose nanofibrils forms an interconnected network of cellulose extending from the second layer to the intermediate layer.
28. The conductive paper according to any of claims 23 to 27,
wherein the electrically conductive nanostructured material comprises a plurality of nanostructures.
29. The conductive paper according to claim 28,
wherein the nanostructures form an interconnected network extending from the first layer to the intermediate layer.
30. The conductive paper according to any of claims 28 to 29,
wherein the nanostructures comprise one or more of a group consisting of nanoparticles, nanotubes, nanowires, nanosheets.

31. The conductive paper according to any of claims 28 to 29,
wherein the nanostructures comprise metallic nanowires or semiconductor nanowires.
32. The conductive paper according to any of claims 28 to 29,
wherein the nanostructures comprise carbon nanotubes.
33. The conductive paper according to any of claims 28 to 29,
wherein the nanostructures comprise molybdenum disulphide or tungsten disulphide nanostructures.
34. The conductive paper according to any of claims 23 to 33,
wherein the electrically conductive nanostructured material comprises semiconducting nanostructured material.
35. The conductive paper according to any of claims 23 to 34,
wherein the first layer, the second layer and the intermediate layer further comprises a light scattering reduction material.
36. The conductive paper according to claim 35,
wherein the light scattering reduction material is a polymeric material.
37. The conductive paper according to claim 35 or claim 36,
wherein the light scattering reduction material is polydimethylsiloxane.
38. An electrochromic paper comprising:
the conductive nanopaper according to any of claims 22 to 37; and
an electrochromic material on the conductive nanopaper.

39. The electrochromic paper according to claim 38,
wherein the electrochromic material comprises a plurality of electrochromic nanostructures anchored to the conductive nanopaper.
40. The electrochromic paper according to claim 38 or claim 39,
wherein the electrochromic material comprises tungsten oxide.