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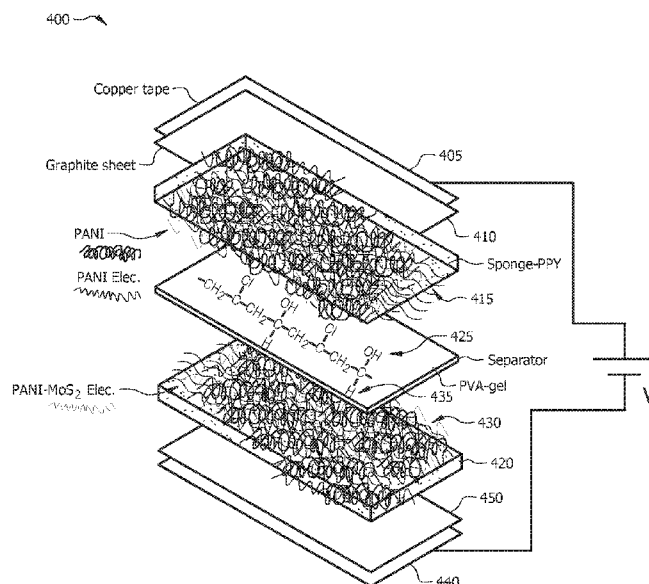


FIG. 4

(57) Abstract: A novel electrode and associated method of manufacturing said novel electrode comprising a porous structure having absorbed polystyrene sulfonate (PSS), a self-assembled polypyrrole (PPy) layer adjacent to the PSS absorbed porous structure, a self-assembled polyaniline (PANI) layer adjacent to the PPy layer, an electrochemically deposited PANI layer adjacent to the PPy layer and an electrochemically deposited PANI-molybdenum disulfide (PANI-MoS₂) layer adjacent to the electrochemically deposited PANI layer. A supercapacitor and associated method of manufacturing a supercapacitor comprising a first novel electrode and a second novel electrode separated by a polyvinyl gel and a porous separator.



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5 HIGH SPECIFIC CAPACITANCE SOLID STATE 20 SUPERCAPACITOR AND METHOD OF MANUFACTURE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to co-pending U.S. Provisional Patent Application 62/567,425,
10 filed October 3, 2017 and entitled "High Specific Capacitance in Solid State Supercapacitor",
which is herein incorporated by reference in its entirety.

BACKGROUND OF INVENTION

Supercapacitors have been one of the emerging energy storage technologies with potential
applications in small electronics, hybrid vehicles, solar and wind farms. The key factors in a
15 supercapacitor are specific capacitance, specific power, and specific energy which are all
largely dependent upon the nature of electrode materials. To obtain high performance in a
supercapacitor, the electrodes of the device have to be porous with high surface to volume
ratio and high conductivity. Also, for employing the pseudocapacitive effect for enhancing a
device capacitance, the electrode material should present an excellent electrochemical redox
20 stability at a wide potential window. High specific capacitances have been reported in devices
made of nanocomposites of a conducting polymer with graphene, MoS₂, and carbon
nanotubes.

A practical method to enhance the porosity of the electrodes is to coat the composite
materials on the surface of a cellulose or sponge structure, such as a solid-state
25 supercapacitor fabricated with large surface area based carbon nanotubes on bacterial
nanocellulose in poly(styrene-block-ethylene oxide-block-styrene) based ionic liquid
electrolyte. The electrodes based on carbon nanotubes on bacterial nanocellulose had a
specific capacitance of (50 F g⁻¹). Porous nitrogen doped carbon fibers showed a specific
capacitance of 202 F g⁻¹. A volumetric capacitance of 2.5 F cm⁻³ in a solid-state
30 supercapacitor based on carbon fiber and manganese oxide core-shell fiber electrode have
also been demonstrated. Graphene meso and microporous aerogels-based supercapacitor
showed a specific capacitance of 325 F g⁻¹ in a sulfuric-based electrolyte. A supercapacitor
fabricated on a 3D sponge like nano-structure coated with functionalized multi-walled carbon
nanotubes had an energy density of 7.1 Wh kg⁻¹ and a power density of 48 kW kg⁻¹ in an ionic
35 liquid-based electrolyte. A power density of 63 kW kg⁻¹ and energy density of 31 Wh kg⁻¹ with
a manganese oxide and carbon nanotube sponge-based supercapacitor has also been

- 5 reported. It is also known to fabricate supercapacitors by coating graphene oxide on polyurethane based sponge, resulting in an energy density of 89 W h kg⁻¹.

The common approach with aerogel or sponge-based substrates is to dip the substrate in a conductive ink or to mechanically press a conductive powder (e.g. carbon nanotubes or graphene) to the substrate to make conductive porous electrodes. Despite the simplicity of
10 the process, the electrode conductivity may differ in various parts of the substrate, thereby negatively influencing the properties of a supercapacitor made by such a process.

Accordingly, what is needed in the art is an improved solid-state supercapacitor and associated method for manufacturing a solid-state supercapacitor.

SUMMARY OF THE INVENTION

- 15 In various embodiments, the present invention provides an improved supercapacitor comprising a common sponge which provides a large surface area upon which to fabricate a solid-state supercapacitor. The supercapacitor includes two substantially symmetric electrodes separated by a polyvinyl (PVA) layer. The two electrodes are provided by depositing conducting polypyrrole (PPy) and polyaniline (PANI) on the surface of sponge
20 using in-situ self-assembled polymerization technique, wherein the PPy and PANI layers establish conductivity within the sponge. Subsequently, electrochemical PANI and molybdenum disulfide (MoS₂)-PANI are deposited by electrochemical techniques to form the electrodes. The polyvinyl alcohol (PVA) gel is then synthesized and further, polyaniline, polyaniline-graphene and polypyrrole, polypyrrole graphene are polymerized in PVA gel to
25 obtain highly conducting electrolyte to fabricate the solid-state supercapacitor.

- In one embodiment, an electrode of the present invention includes, a porous structure having absorbed polystyrene sulfonate (PSS), a self-assembled polypyrrole (PPy) layer adjacent to the PSS absorbed porous structure, a self-assembled polyaniline (PANI) layer adjacent to the PPy layer, an electrochemically deposited PANI layer adjacent to the PPy layer and an
30 electrochemically deposited PANI-molybdenum disulfide (PANI-MoS₂) layer adjacent to the electrochemically deposited PANI layer.

The porous structure may be selected from a sponge, an organic sponge, open-cell polyurethane, foam, polystyrene, wood, honeycomb ceramics, coral, pumice, porous ceramics and aerogel.

- 35 Additionally, the PANI layers may include one or more of, PANI-dichalcogenide, polyaniline derivatives (poly-toluidine, poly(ortho-anisidine), poly(methyl aniline), poly(ortho-ethoxyaniline) and its derivatives, polythiophene 'PTh', polyethylenedioxythiophene (PEDOT),

- 5 polyhexylthiophene (PHTh), conducting methyl substituted polyaniline, conducting polymer copolymer (poly(aniline-pyrrole) conducting polymer nanocomposite films with graphene (G), carbon nanotubes tin oxide, titanium oxide (TiO₂), tungsten oxide (WO₃), nanodiamond, zinc oxide over polyaniline film.

10 In another embodiment, the present invention provides a supercapacitor including a first electrode and a second electrode separated by polyvinyl alcohol (PVA) layer and a separator. The first electrode and the second electrode including a porous structure having absorbed polystyrene sulfonate (PSS), a self-assembled polypyrrole (PPy) layer adjacent to the PSS absorbed porous structure, a self-assembled polyaniline (PANI) layer adjacent to the PPy layer, an electrochemically deposited PANI layer adjacent to the PPy layer and an
15 electrochemically deposited PANI-molybdenum disulfide (PANI-MoS₂) layer adjacent to the electrochemically deposited PANI layer.

The supercapacitor may further include a graphite sheet/copper tape layer adjacent to the PSS porous structure of the first electrode and the second electrode.

20 In another embodiment, the present invention provides a method for manufacturing an electrode which includes, contacting a porous structure with a polyanion solution of polystyrene sulfonate (PSS) to form a porous structure/PSS substrate, performing in-situ self-assembly polymerization of pyrrole (PPy) on the porous structure/PSS substrate to form a porous structure/PSS/PPy substrate, performing in-situ self-assembly polymerization of polyaniline (PANI) on the porous structure/PSS/PPy substrate to form a porous
25 structure/PSS/PPy/PANI substrate, electrochemically depositing a layer of PANI on the porous structure /PSS/PPy/PANI substrate to form a porous structure/PSS/PPy/PANI/PANI substrate and electrochemically depositing a polyaniline molybdenum disulfide (PANI-MoS₂) layer over the porous structure/PSS/PPy/PANI/PANI substrate to form a porous structure/PSS/PPy/PANI/PANI/PANI-MoS₂ electrode.

30 A method for manufacturing a supercapacitor is additionally provided which includes, manufacturing a first electrode and a second electrode by the process including, contacting a porous structure with a polyanion solution of polystyrene sulfonate (PSS) to form a porous structure/PSS substrate, performing in-situ self-assembly polymerization of pyrrole (PPy) on the porous structure/PSS substrate to form a porous structure/PSS/PPy substrate, performing
35 in-situ self-assembly polymerization of polyaniline (PANI) on the porous structure/PSS/PPy substrate to form a porous structure/PSS/PPy/PANI substrate, electrochemically depositing a layer of PANI on the porous structure /PSS/PPy/PANI substrate to form a porous structure/PSS/PPy/PANI/PANI substrate and electrochemically depositing a polyaniline molybdenum disulfide (PANI-MoS₂) layer over the porous structure/PSS/PPy/PANI/PANI

5 substrate to form a porous structure/PSS/PPy/PANI/PANI/PANI-MoS₂ electrode. The method further includes, applying a first polyvinyl (PVA) gel layer to the PANI-MoS₂ layer of the porous structure/PSS/PPY/PANI/PANI/PANI-MoS₂ first electrode, positioning a separator on the PVA gel layer, applying a second PVA gel layer between the separator and the PANI-MoS₂ layer of the porous structure/PSS/PPY/PANI/PANI/PANI-MoS₂ second electrode,
 10 positioning a first graphite sheet covered with copper tape on an exterior side of the first electrode and positioning a second graphite sheet covered with copper tape on an exterior side of the second electrode to form the supercapacitor.

In a particular embodiment, the supercapacitor can be a large surface area based sponge/polystyrene sulfonate (PSS)/polypyrrole (PPY)/polyaniline (PANI)/PANI-molybdenum disulfide (MoS₂)-poly(vinyl alcohol) (PVA)– PANI-MoS₂/PANI/PPY/PSS Sponge based solid
 15 state supercapacitor.

In an additional embodiment, the supercapacitor can be large surface area based sponge/polystyrene sulfonate (PSS)/polypyrrole (PPY)/polyaniline (PANI)/ PANI-molybdenum disulfide (MoS₂)- (PVA-gel & graphene) polymerized with PANI- poly(vinyl alcohol) (PVA) –gel
 20 – PANI-MoS₂/PANI/PPY/ PSSSponge based solid state supercapacitor.

In another embodiment, the supercapacitor can be a large surface area based sponge/polystyrene sulfonate (PSS)/polypyrrole (PPY)/polyaniline (PANI)/ PANI-molybdenum disulfide (MoS₂)- (PVA-gel & graphene) polymerized with PPY- PANI-MoS₂/PANI/PPY/PSS/sponge containing based electrolyte and assembly of solid state
 25 supercapacitor.

In a particular embodiment, the poly(vinyl alcohol) (PVA) gel may be synthesized in acid. The PVA-gel may be mixed with aniline monomer, graphene and later, added with solution containing ammonium perdisulphate dissolved in 1 M HCl. The aniline may be polymerized over PVA-gel and graphene and results into a gel of PVA-PANI-graphene. Similarly, PVA-
 30 PPY-graphene, PVA-polythiophene-graphene, gel can be prepared. The gel can be prepared from one or mixtures of polyvinyl alcohol, poly (vinyl acetate, poly (vinyl alcohol co-vinyl acetate), poly (methyl methacrylate, poly (vinyl alcohol-co-ethylene ethylene), poly (vinyl butyral-co-vinyl alcohol-co-vinyl acetate), polyvinyl butyral, polyvinyl chloride, polystyrene. The combination of each polymer at different proportions can also be used for fabrication of
 35 PVA-gel used for making supercapacitor. The gel mixed polyaniline, polyaniline-graphene and polypyrrole, polypyrrole graphene may be polymerized in PVA gel to obtain highly conducting electrolyte to fabricate the solid state supercapacitor.

In a specific embodiment, wherein the porous structure is a sponge, the electrode can be

- 5 fabricated for such structures as sponge/PSS/PPY/PANI/PPY-MoS₂,
 sponge/PSS/PPY/PPY/PANI-MoS₂, sponge/PSS/PPY/PPY/polythiophene-MoS₂,
 sponge/PSS/PPY/PPY/poly(o-anisidine)-MoS₂, sponge/PSS/PPY/PPY/poly(o-toluidine)-MoS₂,
 sponge/PSS/PPY/PPY/PPY-MoS₂, sponge/PSS/PPY/PPY/poly(o-ethoxyaniline)-MoS₂,
 sponge/PSS/PPY/PPY/substituted -MoS₂, sponge/PSS/PPY/PPY/PPY-PANI-MoS₂,
 10 sponge/PSS/PPY/PPY/PPY-MoS₂, sponge/PSS/PPY/PANI/PPY-MoS₂,
 sponge/PSS/PPY/PANI/substituted PPY-MoS₂, sponge/PSS/PPY/PANI/PPY-WS₂,
 sponge/PSS/PPY/PANI/substituted PANI-WS₂, sponge/PSS/PPY/PANI/PPY-WS₂,
 sponge/PSS/PPY/PANI/substituted PPY-graphene, sponge/PSS/PPY/PANI/PPY-graphene,
 sponge/PSS/PPY/PANI/substituted PANI-Carbon nanotube (CNTs),
 15 sponge/PSS/PPY/PANI/substituted PPY-CNTs, the mixed PPY, PANI and polythiophene or
 mixture layers can be fabricated.

Additionally, sponge/PSS/PPY/PANI/PPY-MoS₂- PVA-gel -MoS₂-PANI/PPY PANI/PPY/PSS/
 sponge symmetric or sponge/PSS/PPY/PANI/PPY-MoS₂- PVA-gel - MoS₂ -PPY/PPY/PSS/
 sponge supercapacitor may be formed. The combinations can be made from the gel mixtures
 20 described above. The PVA-gel consisting of polyaniline and graphene can also be used as
 electrolyte.

Accordingly, in various embodiments the present invention provides for improved electrodes
 and associated supercapacitors formed from said inventive electrodes, thereby providing a
 device exhibiting improved capacitance over other structures known in the art.

25 BRIEF DESCRIPTION OF THE DRAWINGS

For a fuller understanding of the invention, reference should be made to the following detailed
 description, taken in connection with the accompanying drawings, in which:

FIG. 1 is a series of images depicting the steps of electrode fabrication in which PPY, PANI
 and PANI-MoS₂ are deposited over sponge, in accordance with an embodiment of the
 30 present invention.

FIG. 2 is an image depicting the formation of a PVA based gel electrolyte, in accordance with
 an embodiment of the present invention.

FIG. 3 is a series of images depicting the fabrication steps of a sponge-based solid
 supercapacitor, in accordance with an embodiment of the present invention.

FIG. 4 is a schematic of the sponge-based supercapacitor using copper tape/graphite
 sheet/sponge/PSS/PPY/PANI/PANI/PANI-MoS₂/PVA gel/sponge/PSS/PPY/PANI/PANI/
 35

- 5 PANI-MoS₂/graphite sheet/copper sheet, in accordance with an embodiment of the present invention.

FIG. 5A is an SEM image of a pure sponge, in accordance with an embodiment of the present invention.

- 10 FIG. 5B is a magnified image of the SEM image of the pure sponge of FIG. 5A, in accordance with an embodiment of the present invention.

FIG. 5C is an SEM image of a pure sponge/PPy, in accordance with an embodiment of the present invention.

FIG. 5D is a magnified image of the SEM image of the pure sponge/PPy substrate of FIG. 5C, in accordance with an embodiment of the present invention.

- 15 FIG. 5E is an SEM image of a pure sponge/PPy/PANI substrate (via in-situ self-assembly), in accordance with an embodiment of the present invention.

FIG. 5F is a magnified image of the SEM image of the pure sponge/PPy/PANI substrate of FIG. 5E, in accordance with an embodiment of the present invention.

- 20 FIG. 5G is an SEM image of a pure sponge/PPy/PANI/PANI-MoS₂ substrate (via electrochemical deposition), in accordance with an embodiment of the present invention.

FIG. 5H is a magnified image of the SEM image of the pure sponge/PPy/PANI/ PANI-MoS₂ substrate substrate of FIG. 5G, in accordance with an embodiment of the present invention.

FIG. 6A is a graphical illustration of the X-ray diffraction of PPY/PANI/MoS₂, in accordance with an embodiment of the present invention.

- 25 FIG. 6B is a graphical illustration of the FTIR spectra of PPY, PPY/PANI and PPY/PANI/MoS₂ deposited on sponges from 600-2000 cm⁻¹, in accordance with an embodiment of the present invention.

- 30 FIG. 7A is a graphical illustration of the CV as a function of scan rates at (1) 5 mV/s (2) 10 mV/s (3) 20 mV/s (4) 50 mV/s and (5) 100 mV/s, in accordance with an embodiment of the supercapacitor of the present invention.

FIG. 7B is a graphical illustration of the CV of the supercapacitor at 10 mV/s, in accordance with an embodiment of the present invention.

FIG. 7C is a graphical illustration of the specific capacitance of the supercapacitor, estimated

5 using CV studies, in accordance with an embodiment of the present invention.

FIG. 7D is a graphical illustration of the charge/discharge cycling performance of the supercapacitor at 30 mA, in accordance with an embodiment of the present invention.

FIG. 8 is a graphical image depicting CV cycling performance at 20 mV/s for 1000 cycles (inset) CV curves collected at the 1st and the 1000th cycle, in accordance with an embodiment
10 of the supercapacitor of the present invention.

FIG. 9 is a graph depicting leakage current when charging with constant voltage of 1V over a duration of 500 seconds, in accordance with an embodiment of the supercapacitor of the present invention.

FIG. 10A is a graphical image depicting CVs curves as a function of scan rate 5, 10, 20, 50
15 and 100 mV/sec of 2 years old symmetric supercapacitor based on sponge/PSS/PPY/PPY/PPY-MoS₂ electrode materials, in accordance with an embodiment of the supercapacitor of the present invention.

FIG. 10B is a graphical illustration of and PVA-gel as an electrolyte sec (inset) at 10 mV/s, in accordance with an embodiment of the supercapacitor of the present invention.

20 FIG. 11 is a graph depicting Nyquist plots (inset) of the applied equivalent circuit of the sponge supercapacitor, in accordance with an embodiment of the supercapacitor of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In the following detailed description of the preferred embodiments, reference is made to the
25 accompanying drawings, which form a part hereof, and within which are shown by way of illustration specific embodiments by which the invention may be practiced. It is to be understood that other embodiments by which the invention may be practiced. It is to be understood that other embodiments may be utilized, and structural changes may be made without departing from the scope of the invention.

30 While organic sponge, polyurethane and foam-based polystyrene based porous materials are inexpensive, they are also naturally insulating. The present invention transforms a sponge into a nearly metallic conductivity through the deposition of conducting polymer, utilizing both in-situ and electrochemical techniques. In addition to providing the substrate, the sponge also contains the hybrid network within its large surface area, which enables fabrication of a high
35 specific capacitance based supercapacitor. As such, in various embodiments, porous

5 materials, such as wood, foam material, honeycomb ceramics, coral, pumice, porous ceramics, open-cell polyurethane foam, aerogel, etc. can be used to make an inexpensive conducting and solid-state supercapacitor.

In various embodiments, the present invention provides a multilayer structure electrode built on a sponge substrate and a solid-state supercapacitor having a polyvinyl alcohol (PVA) gel-based electrolyte, which utilizes the novel electrode. To build the electrode in-situ, self-assembled polymerization of both PPy and PANI were used to establish a conductive surface for the subsequent electrochemical polymerization of molybdenum disulfide (MoS₂)-PANI nanocomposite to obtain the supercapacitor electrodes. The electrochemical study results are promising toward practical application of the multilayer electrode structure for high power and high energy density supercapacitors.

With reference to FIG. 1, in one embodiment the electrode fabrication steps **100**, utilizing a commercial kitchen sponge are illustrated. In this embodiment, the sponge was washed in deionized water and then dipped in a polyanion solution of polystyrene sulfonate (PSS) (2 mg/ml) for 24 hours to form a sponge/PSS substrate **105**. In a specific embodiment, the sponge may be a high-density foam. The PSS treatment allowed the sponge surface to absorb negative charges of anions.

Next, pyrrole (PPy) was polymerized by in-situ self-assembly polymerization over the PSS treated sponge **105** resulting in a sponge/PSS/PPy substrate **110**. In a particular embodiment, 0.1 M pyrrole and 0.1M para-toluene sulfonic acid were added to a 1M HCl solution, followed by 0.05M iron chloride, which was then stirred for a few seconds. The sponge/PSS substrate was then dipped in the resulting solution and held for 3 hours. The sponge/PSS/PPy was then cleaned and kept in 1M HCl solution.

A layer of polyaniline (PANI) was then deposited on the sponge/PSS/PPy substrate **110** to form a sponge/PSS/PPy/PANI substrate **115**. In a particular embodiment, the PANI was deposited by in-situ self-assembled technique using a solution of 0.2M aniline, 0.1M of an oxidizing agent (ammonium persulfate, APS) in 1M HCl for a duration of 3 hours.

The second layer of PANI was then deposited on the sponge/PSS/PPy/PANI substrate **115** to form a sponge/PSS/PPy/PANI/PANI substrate **120**. In a particular embodiment, the second layer of PANI was deposited by an electrochemical technique in 0.2 aniline in 1 M HCl at a potential of 1.5 V for a duration of 2 hours, for each side of the sponge.

The final layer of PANI-MoS₂ was then electrochemically deposited over the sponge/PSS/PPy/PANI substrate **120** to form a sponge/PSS/PPy/PANI-MoS₂ substrate **125**. In a particular embodiment the PANI-MoS₂ was deposited in an electrochemical cell at 1.5 V

5 in a solution containing 0.2 M aniline, 0.5 g MoS₂, 1g cetrimonium bromide 'CTAB' for a duration of 2 hours. The sponge/PSS/PPy/PANI-MoS₂ substrate was made upside down, and further deposition was also made at 1.5 V for an additional 2 hours to complete the deposition process. These processing steps resulted in a nearly metallic conductivity in the sponge/PSS/PPy/PANI/PANI-MoS₂ layers.

10 FIG. 1 illustrates the steps 100 involved in the electrode fabrication process of the present invention and the chemical structures of the conducting polymer and its composite materials. Following the fabrication steps, the sponge/PSS/PPy/PANI-MoS₂ was cleaned using deionized water, and subsequently in 1 M HCl, and gently squeezed to remove the acid and left to dry at room temperature for 24 hours. The sponge/PSS/PPy/PANI/PANI-MoS₂
15 electrode was subsequently used to characterize and fabricate a solid supercapacitor.

For the preparation of the PVA-gel employed in the solid supercapacitor, 10 g of poly(vinyl alcohol) (PVA) was added to 100 ml of 1M HCl, which was then stirred, under heat at 80°C° for a duration 24 hours. The gel was then allowed to age for one week prior to the fabrication of the supercapacitor. FIG. 2 illustrates the structure 200 of the PVA-gel.

20 FIG. 3 illustrates the methods steps 300 in the fabrication of the sponge-based solid supercapacitor of the present invention. In a first step 305 for the preparation of the supercapacitor, the sponge/PSS/PPy/PANI/PANI-MoS₂ was used for both electrodes 310, 315 in the symmetric supercapacitor structure. The PVA gel electrolyte 320 was applied to the electrodes 310, 315 and a porous filter paper that was used as the separator 330. The
25 electrodes 310, 315, PVA gel 320 and separator 330 were sandwiches together in a second step 340. In a third step 350, a copper tape 365, 370 was used as the current collector for each electrode 310, 315. The completed device 360 was assembled by sandwiching two electrodes 310, 315 and the separator 330 between two layers of plexiglass and tightened with four screws.

30 FIG. 4 illustrates the various layers of the sponge-based solid supercapacitor 400. In this embodiment the supercapacitor 400 includes, in order from top to bottom, a first copper tape layer 405 over a first graphite sheet 410, a first sponge/ PSS/PPy/PANI/PANI-MoS₂ electrode 415, a first PVA gel layer 425 a separator 435, a second PVA gel layer 430, a second sponge/PSS/PPy/PANI/PANI-MoS₂ electrode 420, a second graphite sheet 450 and a second
35 copper tape layer 440.

To analyze the physical and structural characteristics of the solid supercapacitor, field emission scanning electron microscopy (FE-SEM, SU70, at accelerating voltage of 5kV) was used to image the sponge and each deposited conducting polymer, in addition to the

5 composite structure on the sponge. FIG. 5A and FIG. 5B illustrate an SEM image of the pure sponge. FIG. 5C and FIG. 5D present images of the sponge/PPy layer. FIG. 5E and FIG. 5F present images of the sponge/PPy/PANI (via in-situ self-assembly) layer. FIG. 5G and FIG. 5H present images of the sponge/PPy/PANI/PANI-MoS₂ (via electrochemical deposition) layer. The structure of the sponge before and after the PPy layer is different, as shown in
 10 FIG. 5C and FIG. 5D. The smaller magnification shows equally distributed PPy particles approximately 1000 nm to 3500 nm in size. Further, the PANI deposition over PPy changed the structure, whereby nanostructures are clearly visible over the sponge surface as shown in FIG. 5E and FIG. 5F. The PANI-MoS₂ is a clearly distinguishable structure that is different than both PPy and PANI, following the electrochemical deposition. The MoS₂ platelets are
 15 observed in the PANI network in the SEM images of FIG. 5G and FIG. 5H.

A Philips Panalytical Xpert Pro MRD with Cu K α radiation (wavelength = 1.5442 Å) and 2 θ range from 5° to 45° was then used to study the X-ray diffraction (XRD) of sponge/PSS/PPy/PANI-MoS₂. As shown in FIG. 6A, peaks for diffraction angle '2 θ ' at 6.8, 11, 14.4, 33.6, 38 and 40.7 degrees were found in the results. Generally, the emeraldine salt of
 20 PANI is quasi crystalline and PPy is amorphous in nature. However, the composite with MoS₂ structure is ordered state than the conventional PANI as well as PPy structure.

FTIR spectra of sponge/PSS/PPy, sponge/PSS/PPy/PANI and sponge/PSS/PPy/PANI/PANI-MoS₂ was measured using Perkin Elmer spectrometer from 600-2000 cm⁻¹ in the reflectance mode. In FIG. 6B, curve 1 shows the infrared peaks at 1936, 1824, 1726 ((C=N, C-N)), 1586
 25 (C=C stretching), 1494, 1332 (C=N, C-N) bonds, 1242 (N-H plane mode), 1114 (C-H in plane mode), 972 (C-H wag), 833 (C-H wagging), 749 and 694 cm⁻¹ [29]. Curve 2 in FIG. 6B shows the vibrational bands at 1933, 1821, 1722, 1595, 1406, 1332, 1233, 1114, 969, 824, 728, 627 cm⁻¹. Curve 3 in FIG. 6B shows the infrared peaks at 1940, 1822, 1729, 1600, 1490, 1394, 1338, 1215, 1114, 962, 846, 742, 867, 665 and 643 cm⁻¹. As illustrated, there is a decrease in
 30 the wavenumber in IR spectra after PANI was polymerized over PPy, which could be due to formation of some hydrogen bonds in the doped form of PANI. 663 cm⁻¹ is the characteristic shifted peak of MoS₂

To assess the electrochemical characteristics of the sponge-based superconductor device, electrochemical tests, including CV, CCCD and EIS, were conducted using the two-electrode
 35 configuration. FIG. 7A shows the CV curves of the device at different scan rates from 5 mV s⁻¹ to 100 mV s⁻¹. Oxidation and reduction peaks are observed at 0.34V and -0.37V, respectively, for the scan rate of 5 mV s⁻¹. The peaks were shifted to 0.8 V (oxidation) and -0.74V (reduction) at 100 mV s⁻¹ scan rate.

FIG. 7B shows the CV plot at 10 mV s⁻¹ scan rate to show the redox peaks. The visible redox

5 peaks at different scan rates imply the strong charge storage via the pseudo-capacitive effect in addition to the double layer effect. The highest specific capacitance of $\sim 569 \text{ F g}^{-1}$ has been calculated from the 5 mV s^{-1} CV result. FIG. 7C shows the charging and discharging behaviors of the sponge/PSS/PPy/PANI//PANI-MoS₂ supercapacitor with the PVA-gel electrolyte. The specific capacitance, specific power density and specific energy density have
 10 been calculated to be 631.6 F g^{-1} , 475 W kg^{-1} and 79.17 Wh kg^{-1} considering the weight of only electrode material. In order to test the stability of the device in multiple cycles, CV results of 1500 cycles were collected when the scan rate was 100 mV s^{-1} . FIG. 7D shows the Nyquist plot of sponge/PSS/PPy/PANI/PANI-MoS₂ based supercapacitor fabricated using PVA-gel. There is a direct fitting of the Nyquist plot and the value of R1, C1, R2 and CPE1
 15 has been estimated $297.7 \text{ } \mu\text{F}$, $2.0817 \text{ } \Omega$, $5.180 \text{ } \Omega$ and $Aw1 = 3.041$, $P1 = 0.05$ and $n1 = 0.5889$.

FIG. 8 shows a retention of $\sim 94 \%$ CV for cycling performance at 1000 mV s^{-1} for 1500 cycles (inset) CV curves collected at the 1st and the 1000th cycle.

To study the leakage current in the sponge supercapacitor, a constant potential of 1 V was
 20 applied for 500 seconds. By monitoring the charging current at the end of charging cycle, it was 4.5 mA which can be corresponding to the leakage current in the device as shown in FIG. 9. FIG. 10A illustrates CVs curves as a function of scan rate $5, 10, 20, 50$ and 100 mV/sec of symmetric supercapacitor based on 2 years old sponge/PPy/PANI/PANI-MoS₂ electrode materials and PVA-gel as an electrolyte. The cyclability of this 2-year-old
 25 supercapacitor is examined under long-term charge/discharge cycling over 100 cycles, which has shown a good cyclic performance and reversibility as evidenced by FIG. 10B.

FIG. 11 shows the Nyquist plot of sponge/PPy/PANI/PANI-MoS₂ based supercapacitor fabricated using PVA-gel. There is a direct fitting of the Nyquist plot and the value of R1, C1, R2 and CPE1 has been estimated. The C1 $297.7 \text{ } \mu\text{F}$, R1 2.0817 , R2 $= 5.180$, $Aw1 = 3.041$, $P1$
 30 $= 0.05$ and $n1 = 0.5889$.

As described in detail, in various embodiments, the present invention provides a multilayer electrode structure with conducting polymers and a composite material of molybdenum disulfide (MoS₂) that was designed and fabricated on a kitchen sponge substrate to make solid state supercapacitors with a high specific capacitance of 631.6 F g^{-1} .

35 In various embodiments, the sponge-based electrode was fabricated by in-situ self-assembled polymerization of a layer of polypyrrole (PPy) and a layer of polyaniline (PANI) on a sponge substrate. The layers of PPy and PANI converted the sponge surface to a conductive surface that was used for the electrochemical deposition of a thicker layer of PANI

5 and another layer of PANI-MoS₂-PANI composite. The polyvinyl alcohol (PVA) gel was synthesized and further, PANI, was polymerized in PVA gel to obtain highly conducting electrolyte.

The fabrication, characterization and results demonstrate that large surface area based sponge PSS/PPy//PANI/PANI-MoS₂ electrodes may potential use as supercapacitor electrode
10 materials for a promising low-cost supercapacitor which exhibits good electrochemical performance with superior cycle durability, time stability and shelf life.

In the preceding specification, all documents, acts, or information disclosed does not constitute an admission that the document, act, or information of any combination thereof was publicly available, known to the public, part of the general knowledge in the art, or was known
15 to be relevant to solve any problem at the time of priority.

The disclosures of all publications cited above are expressly incorporated herein by reference, each in its entirety, to the same extent as if each were incorporated by reference individually.

It will be seen that the advantages set forth above, and those made apparent from the
20 foregoing description, are efficiently attained and since certain changes may be made in the above construction without departing from the scope of the invention, it is intended that all matters contained in the foregoing description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic
25 and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall there between. Now that the invention has been described,

5 What is claimed is:

1. An electrode comprising:

a porous structure having absorbed polystyrene sulfonate (PSS);

a self-assembled polypyrrole (PPy) layer adjacent to the PSS absorbed porous structure;

10 a self-assembled polyaniline (PANI) layer adjacent to the PPy layer;

an electrochemically deposited PANI layer adjacent to the PPy layer; and

an electrochemically deposited PANI-molybdenum disulfide (PANI-MoS₂) layer adjacent to the electrochemically deposited PANI layer.

15 2. The electrode of claim 1, wherein the porous structure is selected from a sponge, an organic sponge, open-cell polyurethane foam polystyrene, wood, foam, honeycomb ceramics, coral, pumice, porous ceramics and aerogel.

3. The electrode of claim 1, wherein the self-assembled PANI layer further comprises one or more of, PANI-dichalcogenide, polyaniline derivatives (poly-toluidine, poly(ortho-anisidine), poly(methyl aniline), poly(ortho-ethoxyaniline) and its derivatives, polythiophene 'PTh', polyethylenedioxythiophene (PEDOT),
20 polyhexylthiophene (PHT), conducting methyl substituted polyaniline, conducting polymer copolymer (poly(aniline-pyrrole) conducting polymer nanocomposite films with graphene (G), carbon nanotubes tin oxide, titanium oxide (TiO₂), tungsten oxide (WO₃), nanodiamond, zinc oxide over polyaniline film.

25 4. The electrode of claim 1, wherein the electrochemically deposited PANI layer further comprises one or more of, PANI-dichalcogenide, polyaniline derivatives (poly-toluidine, poly(ortho-anisidine), poly(methyl aniline), poly(ortho-ethoxyaniline) and its derivatives, polythiophene 'PTh', polyethylenedioxythiophene (PEDOT), polyhexylthiophene (PHT), conducting methyl substituted polyaniline, conducting
30 polymer copolymer (poly(aniline-pyrrole) conducting polymer nanocomposite films with graphene (G), carbon nanotubes tin oxide, titanium oxide (TiO₂), tungsten oxide (WO₃), nanodiamond, zinc oxide over polyaniline film.

5. A supercapacitor comprising:

a first electrode comprising;

- 5 a porous structure having absorbed polystyrene sulfonate (PSS);
- a self-assembled polypyrrole (PPy) layer adjacent to the PSS absorbed porous structure;
- a self-assembled polyaniline (PANI) layer adjacent to the PPy layer;
- an electrochemically deposited PANI layer adjacent to the PPy layer;
- 10 an electrochemically deposited PANI-molybdenum disulfide (PANI-MoS₂) layer adjacent to the electrochemically deposited PANI layer;
- a second electrode comprising;
- a porous structure having absorbed polystyrene sulfonate (PSS);
- a self-assembled polypyrrole (PPy) layer adjacent to the PSS absorbed porous structure;
- 15 a self-assembled polyaniline (PANI) layer adjacent to the PPy layer;
- an electrochemically deposited PANI layer adjacent to the PPy layer;
- an electrochemically deposited PANI-molybdenum disulfide (PANI-MoS₂) layer adjacent to the electrochemically deposited PANI layer;
- 20 a first polyvinyl alcohol (PVA) layer positioned adjacent to the PANI-MoS₂ layer of the first electrode;
- a second polyvinyl alcohol (PVA) layer positioned adjacent to the PANI-MoS₂ layer of the first electrode; and
- a separator positioned between the first PVA layer and the second PVA layer.
- 25 6. The supercapacitor of claim 5, wherein the porous structure of the first electrode and the second electrode is selected from a sponge, an organic sponge, open-cell polyurethane, foam, polystyrene, wood, honeycomb ceramics, coral, pumice, porous ceramics and aerogel.
7. The supercapacitor of claim 5, wherein the self-assembled PANI layer of the first electrode and the second electrode further comprises one or more of, PANI-dichalcogenide, polyaniline derivatives (poly-toluidine, poly(ortho-anisidine),
- 30

- 5 poly(methyl aniline), poly(ortho-ethoxyaniline) and its derivatives, polythiophene 'PTh', polyethylenedioxythiophene (PEDOT), polyhexylthiophene (PHTh), conducting methyl substituted polyaniline, conducting polymer copolymer (poly(aniline-pyrrole) conducting polymer nanocomposite films with graphene (G), carbon nanotubes tin oxide, titanium oxide (TiO₂), tungsten oxide (WO₃), nanodiamond, zinc oxide over
10 polyaniline film.
8. The supercapacitor of claim 5, wherein the electrochemically deposited PANI layer of the first electrode and the second electrode further comprises one or more of, PANI-dichalcogenide, polyaniline derivatives (poly-toluidine, poly(ortho-anisidine), poly(methyl aniline), poly(ortho-ethoxyaniline) and its derivatives, polythiophene
15 'PTh', polyethylenedioxythiophene (PEDOT), polyhexylthiophene (PHTh), conducting methyl substituted polyaniline, conducting polymer copolymer (poly(aniline-pyrrole) conducting polymer nanocomposite films with graphene (G), carbon nanotubes tin oxide, titanium oxide (TiO₂), tungsten oxide (WO₃), nanodiamond, zinc oxide over polyaniline film.
9. The supercapacitor of claim 5, wherein the first electrode and the second electrode further comprises a copper tape layer adjacent to the PSS porous structure.
20
10. The supercapacitor of claim 9, wherein the first electrode and the second electrode further comprises a graphic sheet layer adjacent to the copper tape layer.
11. The supercapacitor of claim 5, wherein the separator is a porous filter paper.
12. The supercapacitor of claim 5, wherein the PVA gel further comprise graphene.
25
13. A method for manufacturing an electrode, the method comprising:
- contacting a porous structure with a polyanion solution of polystyrene sulfonate (PSS) to form a porous structure/PSS substrate;
- performing in-situ self-assembly polymerization of pyrrole (PPy) on the porous
30 structure/PSS substrate to form a porous structure/PSS/PPy substrate;
- performing in-situ self-assembly polymerization of polyaniline (PANI) on the porous structure/PSS/PPy substrate to form a porous structure/PSS/PPy/PANI substrate;
- electrochemically depositing a layer of PANI on the porous structure /PSS/PPy/PANI substrate to form a porous structure/PSS/PPy/PANI/PANI substrate; and

- 5 electrochemically depositing a polyaniline molybdenum disulfide (PANI-MoS₂) layer over the porous structure/PSS/PPy/PANI/PANI substrate to form a porous structure/PSS/PPy/PANI/PANI/PANI-MoS₂ electrode.
14. The method of claim 13, wherein the porous structure is selected from a sponge, an organic sponge, open-cell polyurethane foam polystyrene, wood, foam, honeycomb
10 ceramics, coral, pumice, porous ceramics and aerogel.
15. The method of claim 13, wherein the self-assembled PANI layer further comprises one or more of, PANI-dichalcogenide, polyaniline derivatives (poly-toluidine, poly(ortho-anisidine), poly(methyl aniline), poly(ortho-ethoxyaniline) and its derivatives, polythiophene 'PTh', polyethylenedioxythiophene (PEDOT),
15 polyhexylthiophene (PHT), conducting methyl substituted polyaniline, conducting polymer copolymer (poly(aniline-pyrrole) conducting polymer nanocomposite films with graphene (G), carbon nanotubes tin oxide, titanium oxide (TiO₂), tungsten oxide (WO₃), nanodiamond, zinc oxide over polyaniline film.
16. The method of claim 13, wherein the electrochemically deposited PANI layer further
20 comprises one or more of, PANI-dichalcogenide, polyaniline derivatives (poly-toluidine, poly(ortho-anisidine), poly(methyl aniline), poly(ortho-ethoxyaniline) and its derivatives, polythiophene 'PTh', polyethylenedioxythiophene (PEDOT), polyhexylthiophene (PHT), conducting methyl substituted polyaniline, conducting polymer copolymer (poly(aniline-pyrrole) conducting polymer nanocomposite films
25 with graphene (G), carbon nanotubes tin oxide, titanium oxide (TiO₂), tungsten oxide (WO₃), nanodiamond, zinc oxide over polyaniline film.
17. A method of manufacturing a supercapacitor, the method comprising:
- manufacturing a first electrode and a second electrode by the process comprising:
- 30 contacting a porous structure with a polyanion solution of polystyrene sulfonate (PSS) to form a porous structure/PSS substrate;
- performing in-situ self-assembly polymerization of pyrrole (PPy) on the porous structure/PSS substrate to form a porous structure/PSS/PPy substrate;
- 35 performing in-situ self-assembly polymerization of polyaniline (PANI) on the porous structure/PSS/PPy substrate to form a porous structure/PSS/PPy/PANI substrate;

- 5 electrochemically depositing a layer of PANI on the porous structure
 /PSS/PPy/PANI substrate to form a porous structure/PSS/PPy/PANI/PANI
 substrate; and
- electrochemically depositing a polyaniline molybdenum disulfide (PANI-MoS₂)
 layer over the porous structure/PSS/PPy/PANI/PANI substrate to form a
10 porous structure/PSS/PPy/PANI/PANI/PANI-MoS₂ electrode;
- applying a first polyvinyl (PVA) gel layer to the PANI-MoS₂ layer of the porous
 structure/PSS/PPY/PANI/PANI/PANI-MoS₂ first electrode;
- positioning a separator on the PVA gel layer;
- applying a second PVA gel layer between the separator and the PANI-MoS₂ layer of
15 the porous structure/PSS/PPY/PANI/PANI/PANI-MoS₂ second electrode;
- positioning a first graphite sheet covered with copper tape on an exterior side of the
 first electrode; and
- positioning a second graphite sheet covered with copper tape on an exterior side of
 the second electrode to form the supercapacitor.
- 20 18. The method of claim 17, wherein the porous structure of the first electrode and the
 second electrode is selected from a sponge, an organic sponge, open-cell
 polyurethane form polystyrene, wood, foam, honeycomb ceramics, coral, pumice,
 porous ceramics and aerogel.
19. The method of claim 17, wherein the separator is a porous filter paper.
- 25 20. The method of claim 17, wherein the PVA gel further comprise graphene.

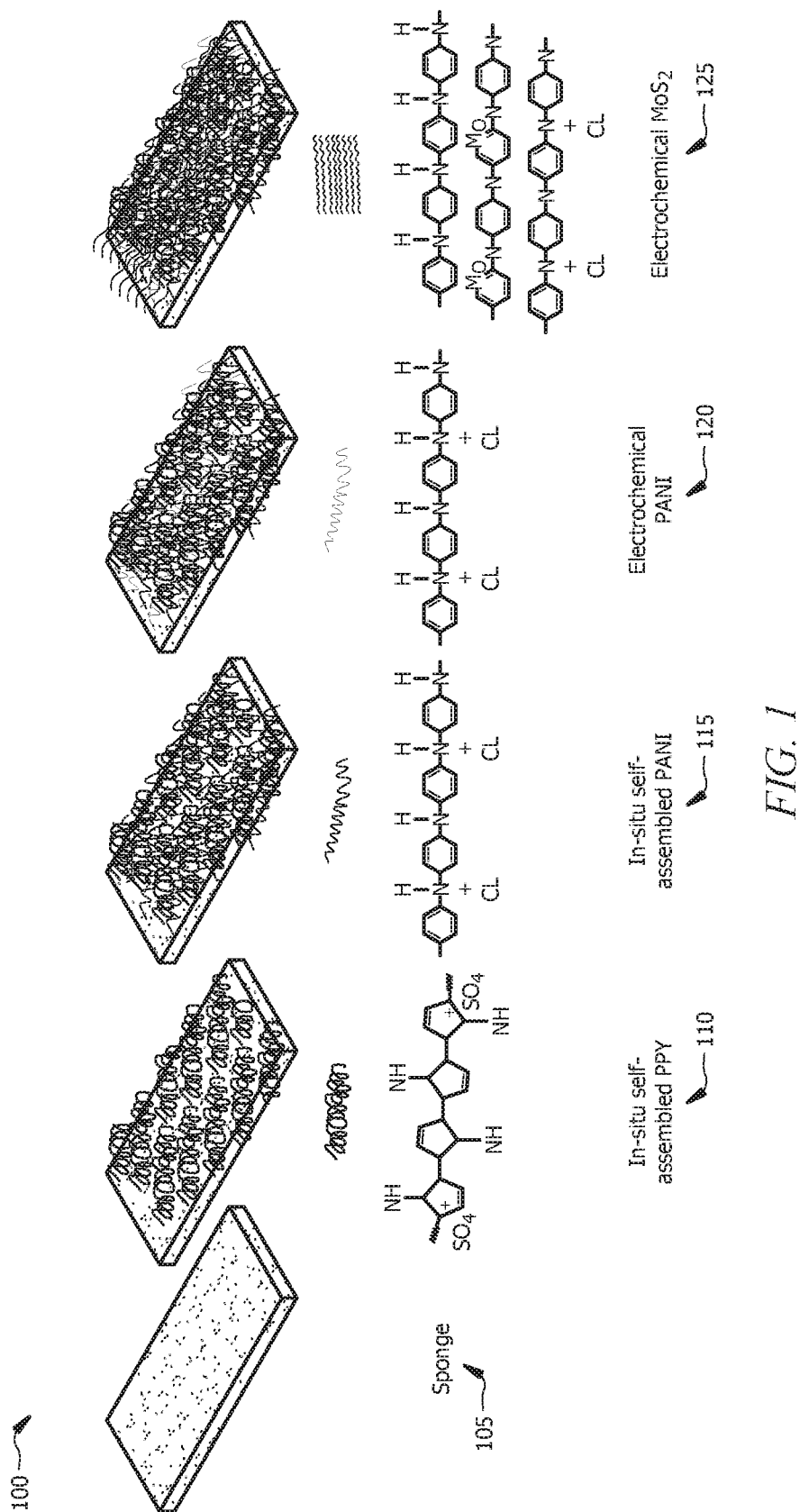


FIG. 1

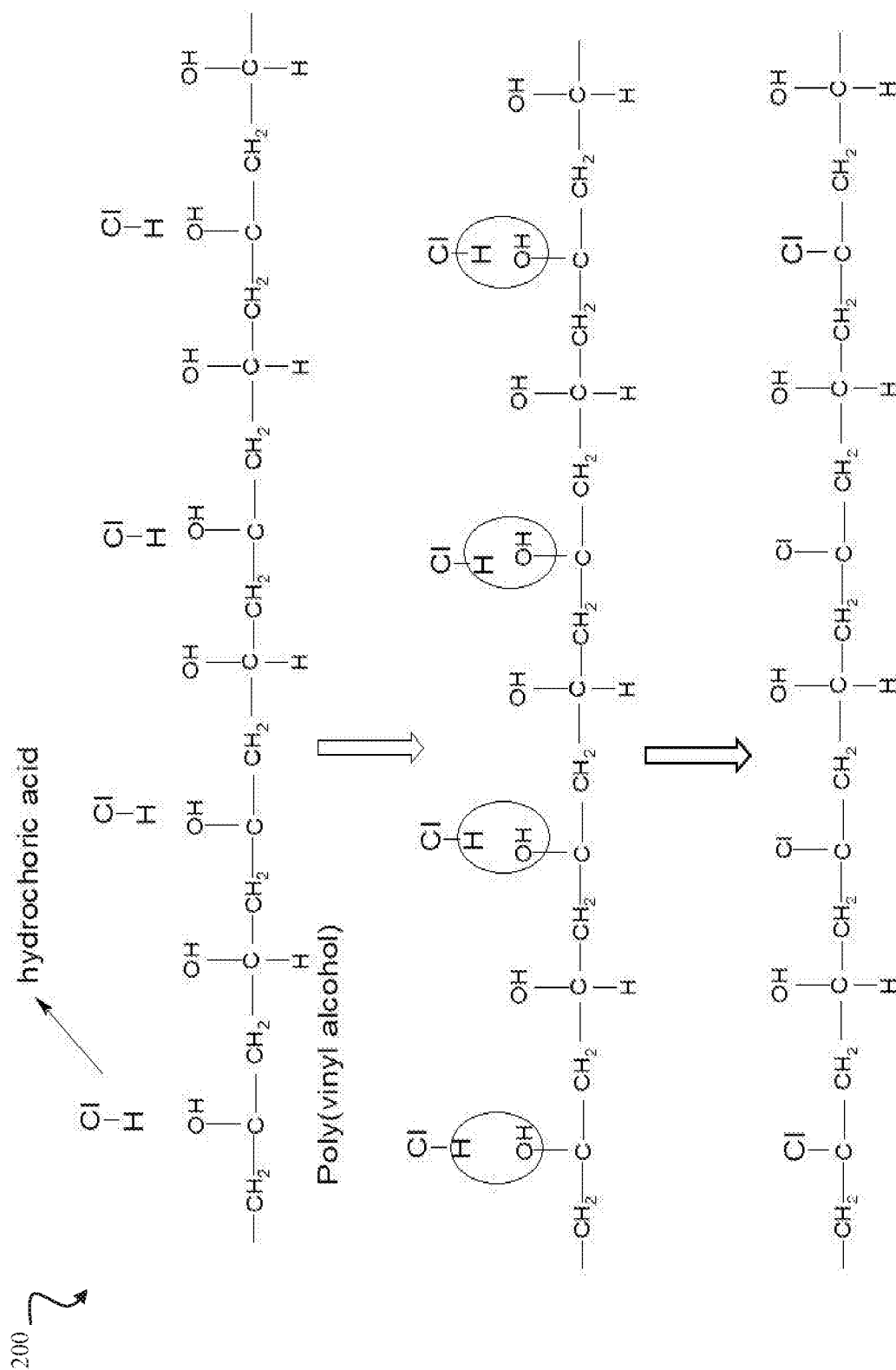


FIG. 2

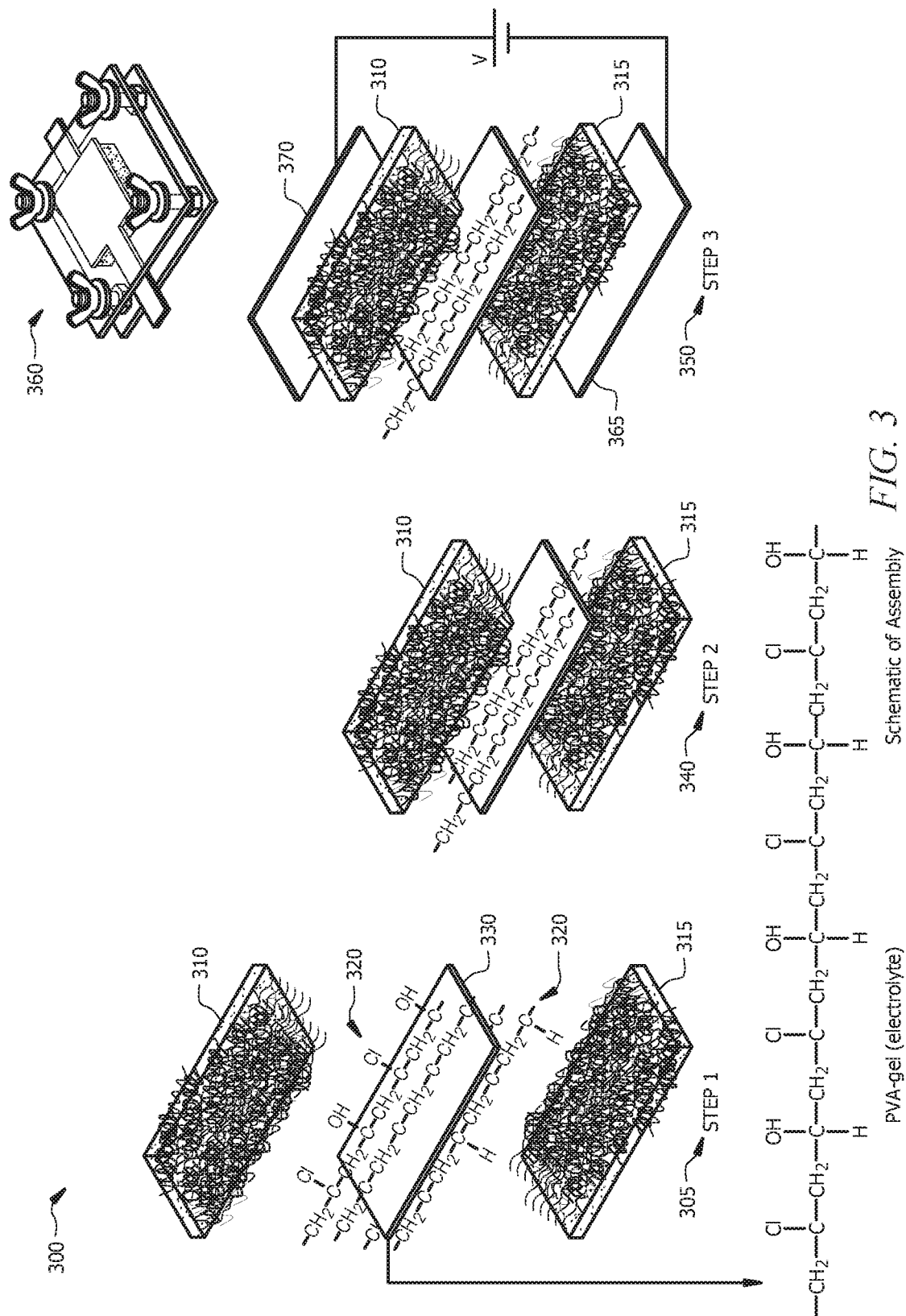


FIG. 3

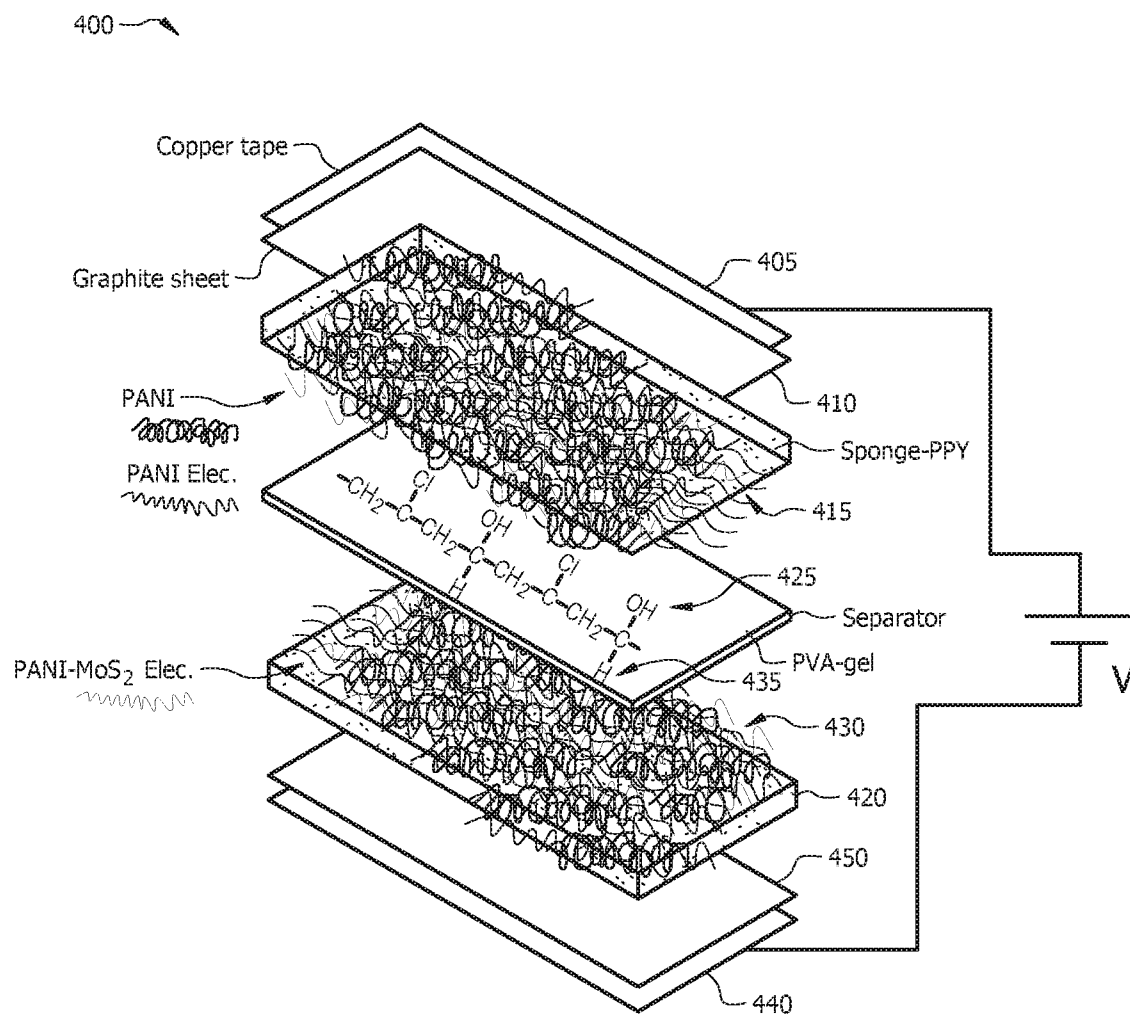


FIG. 4

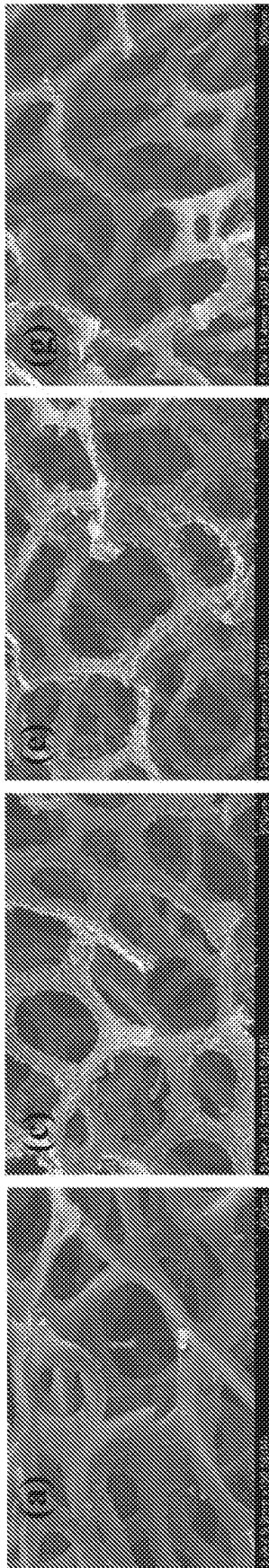


FIG. 5A

FIG. 5C

FIG. 5E

FIG. 5G

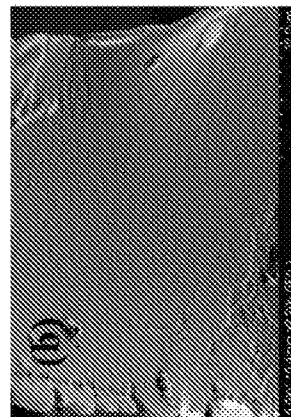


FIG. 5B

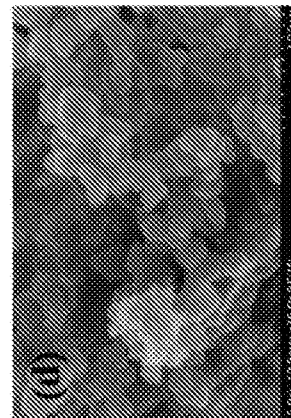


FIG. 5D

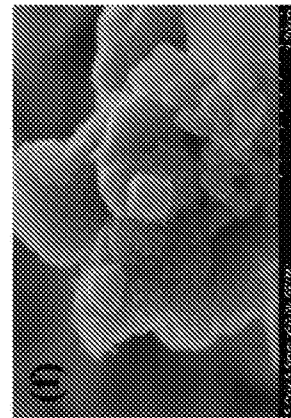


FIG. 5F

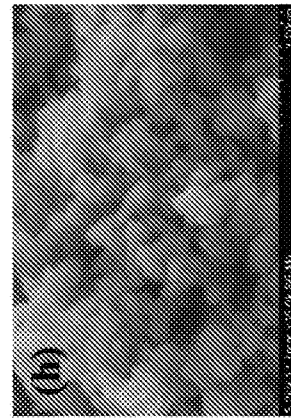


FIG. 5H

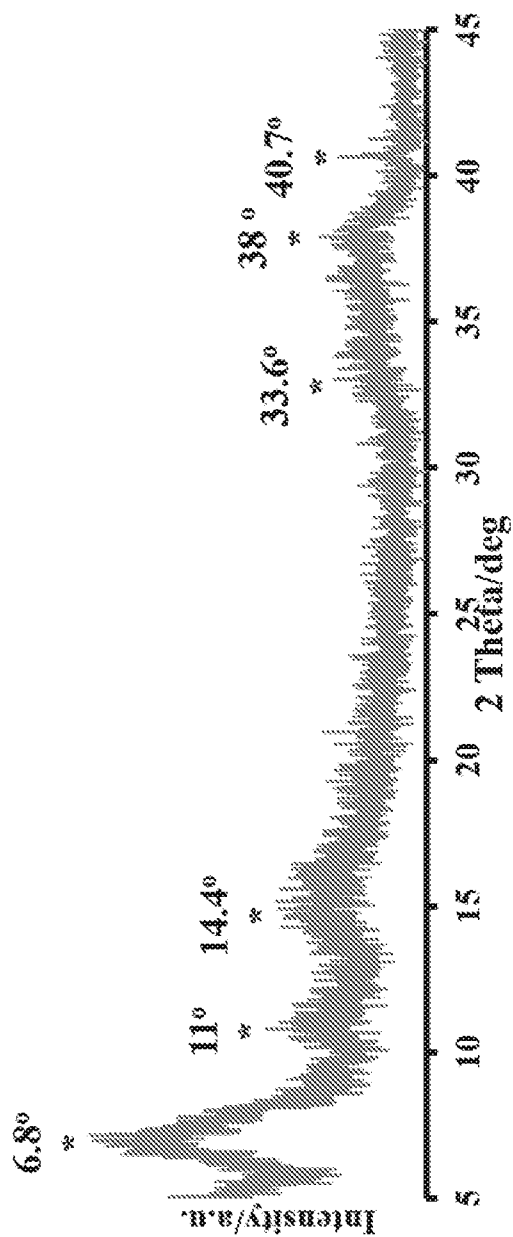


FIG. 6A

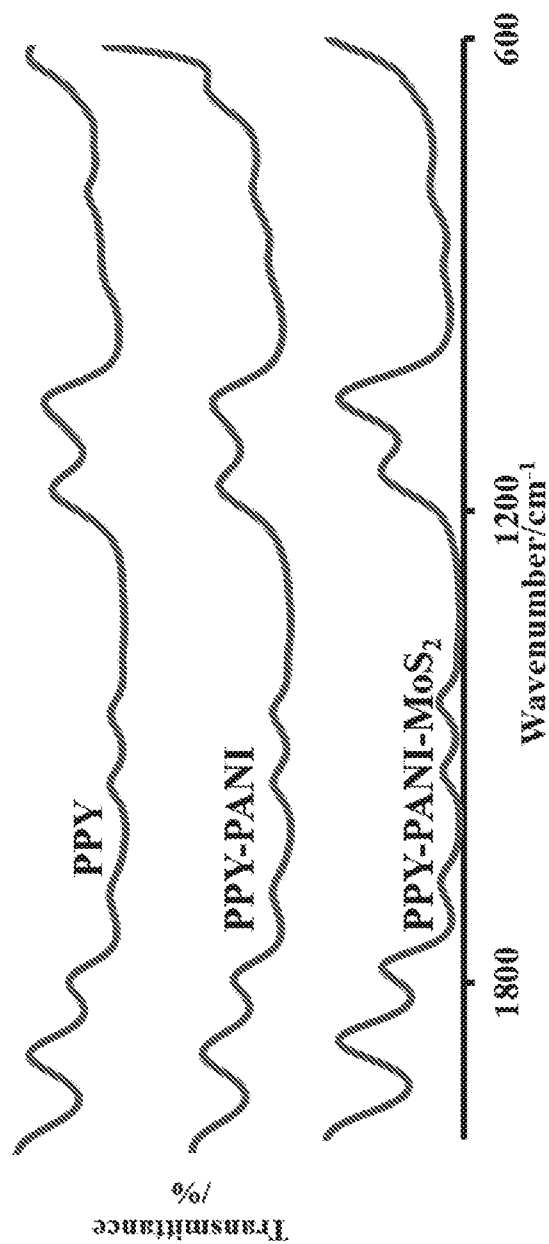
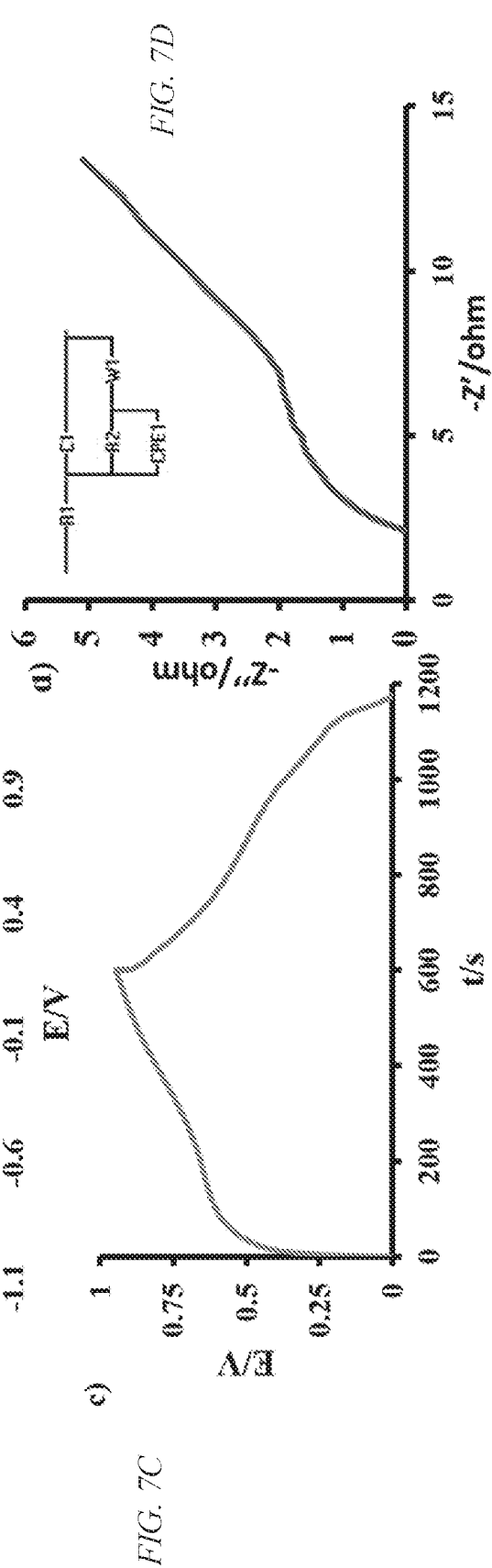
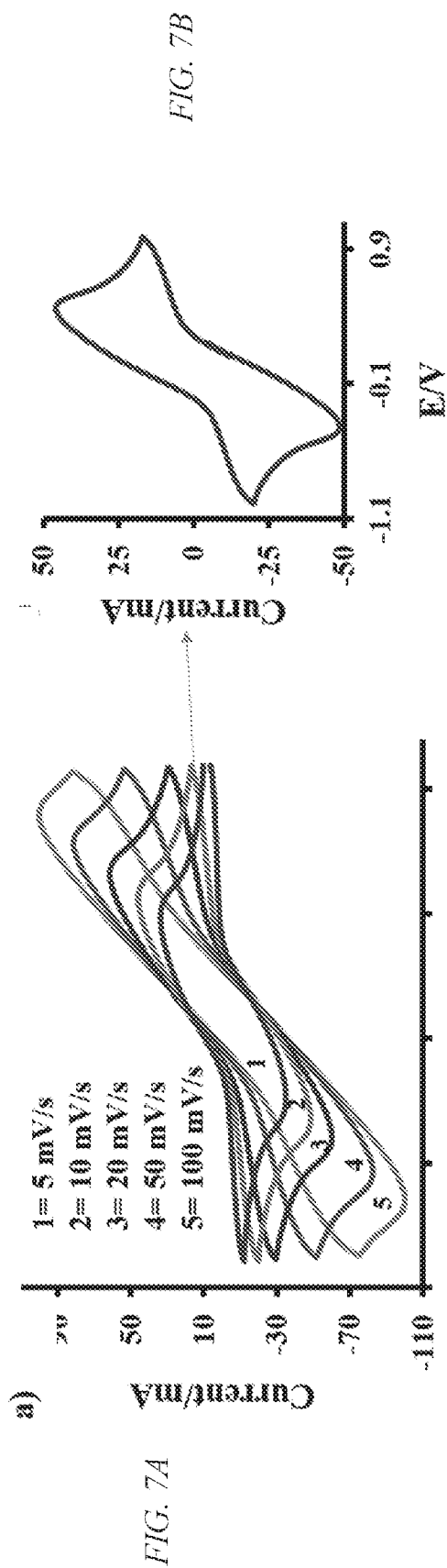


FIG. 6B



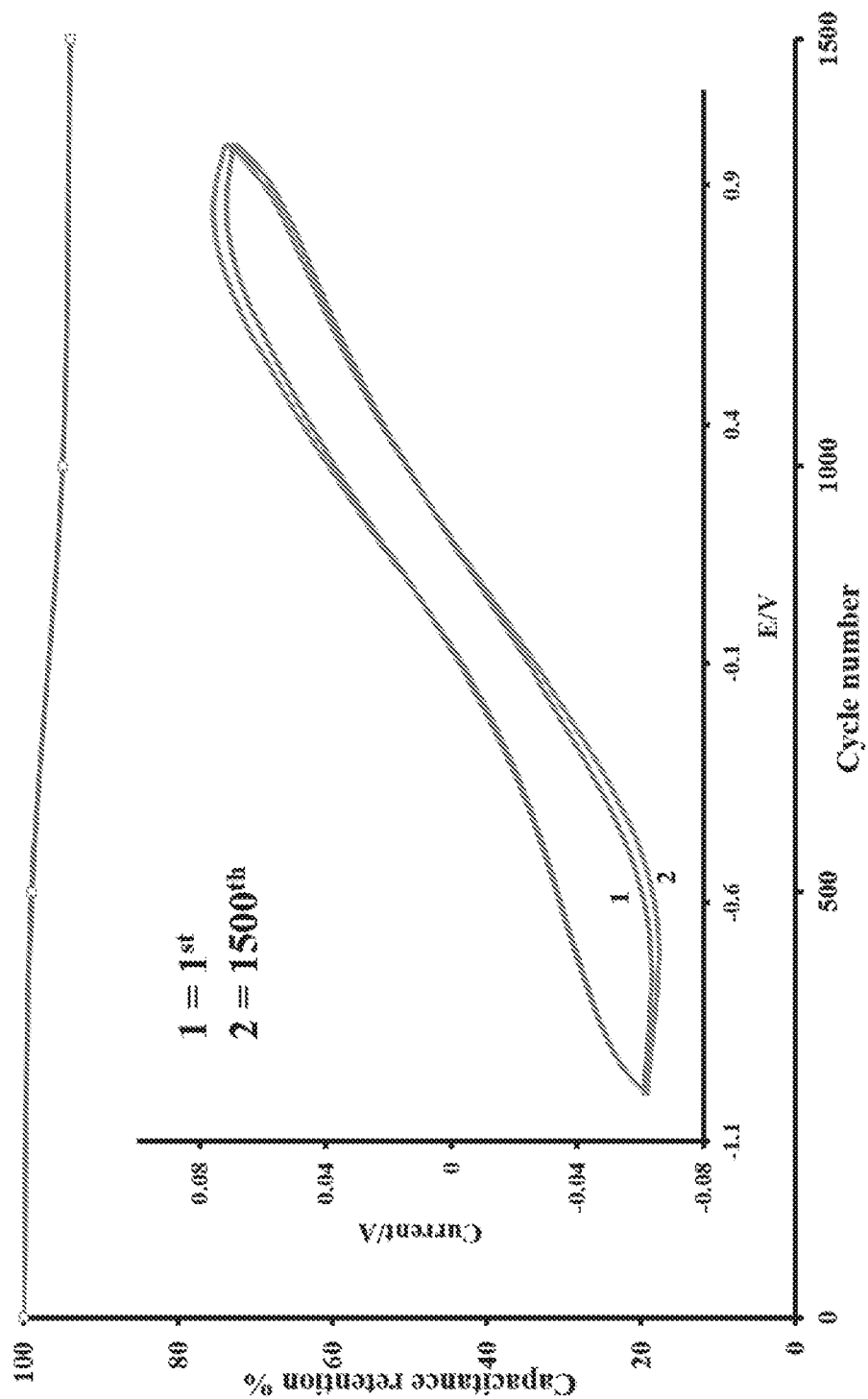


FIG. 8

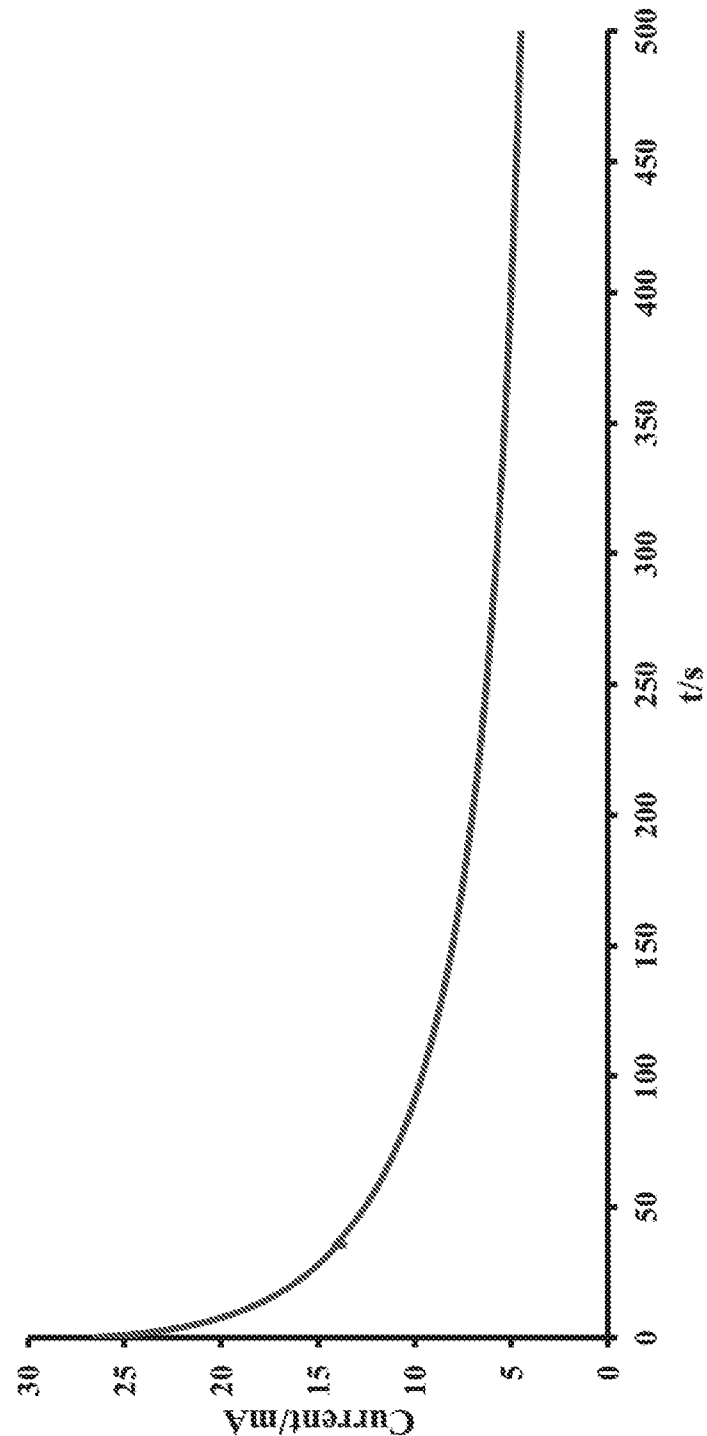


FIG. 9

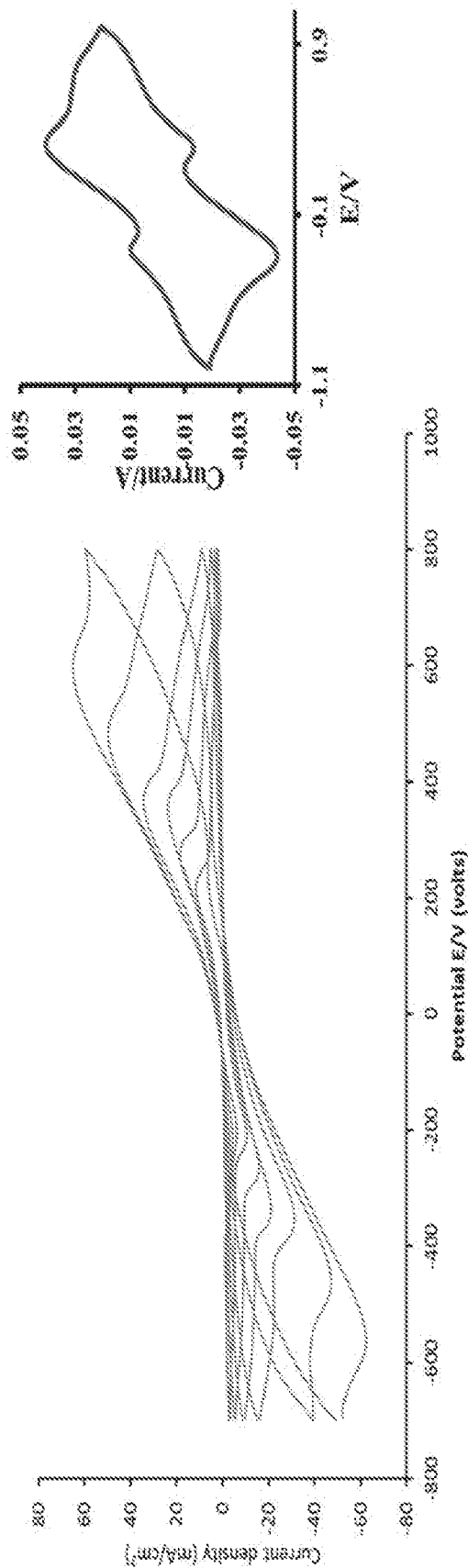


FIG. 10A

FIG. 10B

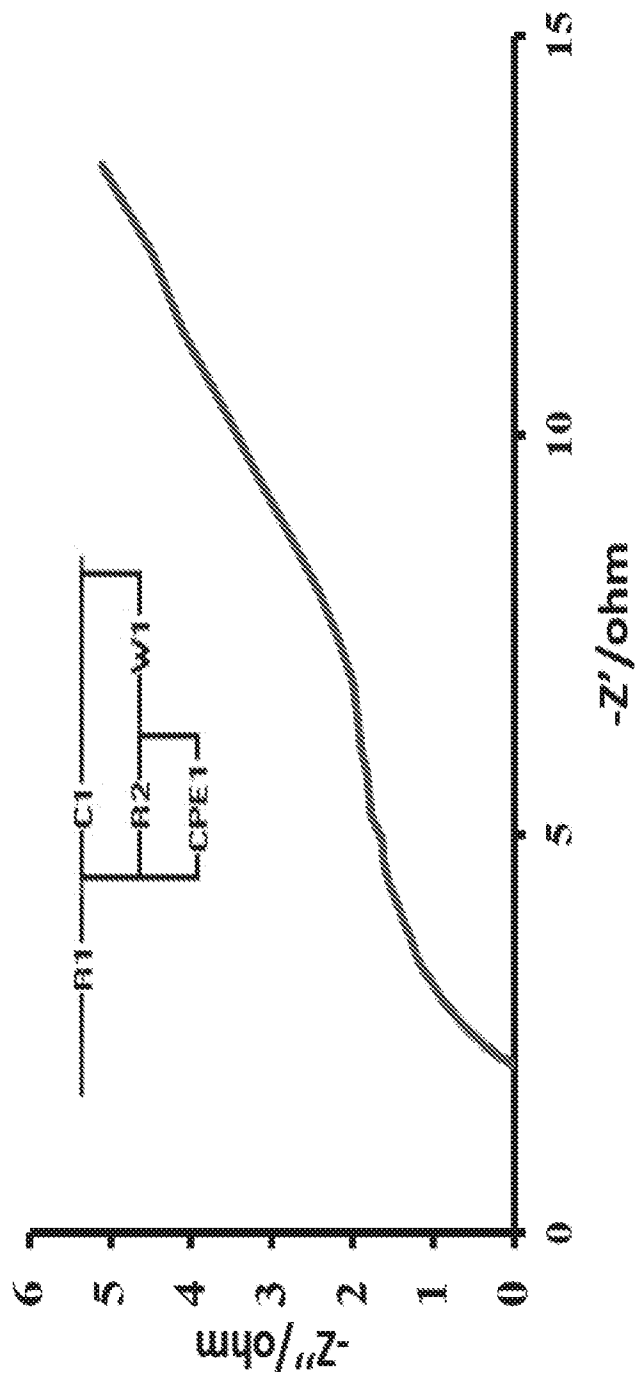


FIG. 11

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/54112

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01L 21/02; H01L 21/4763; H01L 29/24 (2018.01)

CPC - H01L 21/02422; H01L 21/02568; H01L 21/02628; H01L 21/47635; H01L 29/24; H01L 29/45

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)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WANG et al, 'Constructing a "Pizza-Like" MoS ₂ /Polypyrrole/Polyaniline Ternary Architecture with High Energy Density and Superior Cycling Stability for Supercapacitors', Advanced Materials and Interfaces, volume 3, article #1600665, 22 August 2016 (22.08.2016), pg 1-9.	1-20
A	ZHANG et al, 'Electrosynthesis and capacitive performance of polyaniline-polypyrrole composite', Polymer Composites, volume 32, Issue 1, 30 November 2010 (30.11.2010), pg 1-5.	1-20
A	US 2016/0055983 A1 (COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH), 25 February 2016 (25.02.2016), para [0015]-[0025], [0031]-[0035], [0041]-[0045], [0080]-[0083], [0087].	1-20
A	US 7,508,650 B1 (BLUVSTEIN et al), 24 March 2009 (24.03.2009), entire document.	1-20
A	US 9,048,029 B2 (MASSACHUSETTS INSTITUTE OF TECHNOLOGY), 2 June 2015 (02.06.2015), entire document.	1-20

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 November 2018

Date of mailing of the international search report

14 DEC 2018

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