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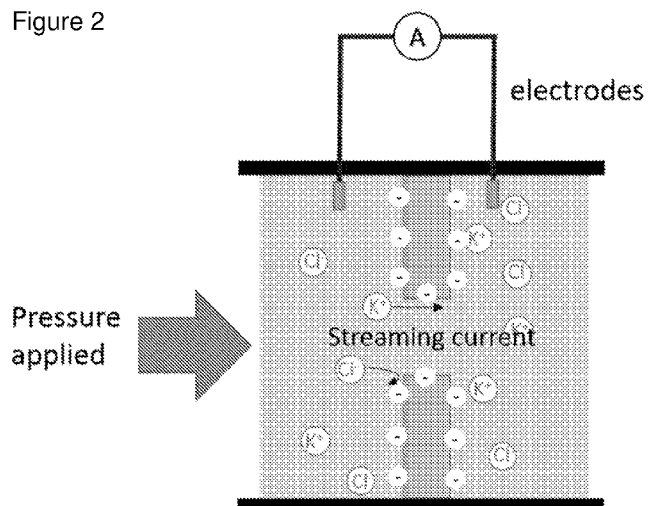
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## (54) Title: MECHANICAL ENERGY HARVESTER

Figure 2



(57) Abstract: The present invention relates to a device for generating a current, comprising: at least two chambers partitioned by a membrane, each chamber housing an electrolyte; the membrane being a 2D membrane, and comprising at least one nano-sized pore permitting the passage of at least one ionic species contained in said electrolyte across the membrane; and means for applying a pressure gradient to at least one of the chambers, for transporting said ionic species across the membrane, wherein the transport of said ionic species generates a current. The present invention further relates to the use of such a device for converting mechanical energy into electricity for immediate use or for storage. The device may also act as a sensor.



## Description

### MECHANICAL ENERGY HARVESTER

#### 5   **Cross-Reference to Related Applications**

This application claims the benefit of priority of Singapore patent application No. 10202000705R, filed on 23 January 2020, its contents being hereby incorporated by reference in its entirety.

#### **Technical Field**

10   The present invention generally relates to a device for converting energy into electrical energy for use or storage.

#### **Background Art**

The search for a source of clean energy has led to the development of nanostructured materials for use in clean energy harvesting assemblies. For  
15   instance, microelectromechanical systems (MEMS) piezoelectric materials, which allow the accumulation of electric charge in solid thin film piezoelectric materials have been widely studied due to its ability to harvest mechanical energy for conversion to electrical energy. The theoretical energy conversion efficiency of  
20   such MEM piezoelectric systems is reported to be about 30%.

In recent years, there has been an increasing interest in harnessing energy that exists in fluidic systems to satisfy the growing energy demand. The discovery of electrokinetic phenomenon such as electroosmotic flow and streaming currents  
25   has aided the development of microfluidic systems which rely on these principles to generate currents which can then be converted into electrical energy. For instance,

glass or silicon-based fluidic systems (e.g., PDMS) have been previously described in the art. These substrates typically comprise nanopatterns or pores through which a fluid may be passed using an applied pressure gradient. The passage of the fluid across the nanopores or nanopatterns disrupts the ionic equilibrium and  
5 leads to a potential difference across at the liquid interface of the nanopore, thereby generating a streaming current.

Nanoporous membranes and materials comprising nanochannels, micro or nanopores of various geometries have been developed extensively for the  
10 conversion of electrokinetic energy. However, the energy conversion efficiency or power density of fluidic devices comprising these materials are often inferior to the solid state MEMS piezoelectric materials. Commercialization of such fluidic devices is further hindered by the cumbersome and tedious manufacture process of such materials

15 Accordingly, there is a need to provide an electrokinetic energy conversion device that overcomes, or at least ameliorates, one or more of the disadvantages described above. In particular, there is a need to provide a device for generating electrical current which demonstrates an improved energy conversion efficiency  
20 and power density over other fluidic and solid state electrokinetic devices in the art.

### Summary of Invention

According to a first aspect, there is provided a device for generating a current, comprising: at least two chambers partitioned by a 2D membrane, each chamber  
25 housing an electrolyte; the membrane comprising at least one nano-sized pore permitting the passage of at least one ionic species contained in said electrolyte across the membrane; and means for applying a pressure gradient to at least one of the

chambers, for transporting said ionic species across the membrane, wherein the transport of said ionic species generates a current.

Advantageously, the present invention provides a readily scalable device for harvesting mechanical energy and transforming the same into electrical energy. Furthermore, the device may be fabricating using readily available materials, which provides a cost-effective alternative to existing electrokinetic devices. Furthermore, the modular nature of the present invention potentially allows it to be retrofitted with a variety of common daily products or structures, thereby providing an alternative source of energy, which is both ecologically friendly and environmentally sustainable. Moreover, it has been found that the provision of a 2D material as the porous membrane significantly improved the conductance of the device and resulted in superior energy conversion efficiencies when compared to currently available technologies.

### Definitions

The following words and terms used herein shall have the meaning indicated:

The term '2D nanopore' is to be interpreted broadly to include apertures, holes, and openings which have a thickness or depth of a single atomic layer.

The term '2D materials' or 'monolayer materials' and grammatical variants thereof is to be interpreted broadly to include materials which consisting of a single layer of atoms. Non limiting examples of such materials include transition metal dichalcogenide, graphene and hexagonal boron nitride materials.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

- 5 As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.
- 10 Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as
- 15 individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.
- 20 Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically
- 25 recited herein.

**Detailed Disclosure of Embodiments**

Exemplary, non-limiting embodiments of a device according to the present invention shall be further disclosed in the following.

5 The at least two chambers of the device may be made of metal, polymer such as plastic or any other suitably robust solid material. Such material is preferably chemically inert with respect to the electrolyte. The at least two chambers used may be substantially sealed or enclosed to prevent any leakage of the electrolyte. In embodiments, the at least two chambers may also be electrically isolated.

10 The 2D membrane as disclosed herein may be a porous membrane having one or a plurality of pores or through holes, which extend substantially throughout the entire thickness of the membrane. The membrane may be a monolayer membrane or a multi-layer membrane having a thickness of less than 20 nm. Each monolayer may comprise atoms covalently bonded in a planar or sheet-like configuration.

15 In embodiments, the membrane may comprise from 1 to about 50 layers of a 2D material, e.g., 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40 and 50 layers. It is to be understood that the porous membrane may have any number of layers between 1 and 50 layers other than shown above. In one embodiment, the porous membrane comprises only a monolayer or a single layer of the 2D material. When the porous membrane has 2 or more layers, the layers may be stacked on upon another or  
20 arranged in a pile.

The overall thickness of the porous membrane may be less than 20 nm. In embodiments, the thickness of the membrane may be provided in the range of from 0.3 nm to 19.9 nm, e.g., 0.35 nm, about 0.5 nm, about 1 nm, about 2 nm, about 3 nm, about 4 nm, about 5 nm, about 6 nm, about 7 nm, about 8 nm, about 10 nm, about 15  
25 nm. The thickness of the membrane may be adjusted as necessary to achieve a

desired level of permeability of the ionic species. The thickness of the porous membrane may correspond to, and may also be defined as, the length of the pore(s).

The porous membrane may comprise at least two surfaces, each surface being respectively exposed to or placed in contact with an electrolyte medium housed in one of the two chambers being partitioned by said membrane. Each membrane surface may be independently positively charged, negatively charged, or is neutral in charge.

The pores in the membrane may be nano-sized pores ("nanopores") and may have a diameter in the range of from 2 nm to 50 nm such as about 2 nm, about 3 nm, about 4 nm, about 5 nm, about 6 nm, about 7 nm, about 8 nm, about 9 nm, about 10 nm, about 11 nm, about 12 nm, about 15 nm, about 20 nm, about 25 nm, about 30 nm, about 35 nm, about 40 nm, about 45 nm, or about 50 nm. In a preferred embodiment, the pore diameter may be equal to or less than 10 nm. The size of the nanopore may be selected in synergistic combination with the concentration of the electrolyte salt. For instance, it was found that nanopore(s) having average diameter of between 5 to 15 nm may provide unexpectedly good conductance when paired with an electrolyte salt having concentrations of 0.1 M or higher. This may be due to an "edge focusing effect", wherein the relatively higher concentration of ions in the electrolyte results in a higher volume charge density of ions localized close to the edge of the pore(s). It may be appreciated that the above "edge focusing effect" may occur at a different concentration for a different diameter of nanopore(s).

It was also found that smaller nanopores may generally result in higher energy conversion efficiency. The thickness of the membrane relative to the diameter size of the nanopore may be termed as the Length-to-diameter ratio of the nanopores. This ratio may be adjusted for optimizing conductance or conversion efficiency and may vary from about 0.01 to about 10, such as 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 1.0, 1.5, 2, 3, 4, 5, 6, 7, 8, 9 or 10.

The membrane may comprise or may be substantially composed of, a material selected from the group consisting of: graphene, monolayer graphene, hexagonal boron nitride, transition metal dichalcogenides ("TMD"), covalent organic frameworks, M-xenes (with M being a transition metal), clays and metal-organic frameworks. In one  
5 embodiment, the membrane of the disclosed device comprises, or is substantially composed of, tungsten disulfide ( $WS_2$ ).

Where the 2D membrane comprises a tungsten disulfide ( $WS_2$ ) monolayer, the covalent bonds between tungsten and sulfur atoms may be broken and upon contact of the porous membrane with an aqueous ionic solution, unpaired sulfur ions are formed.

10 The accumulation of the sulfur ions may thus create a negatively charged surface at the edge of the nanopore. The surface of  $WS_2$  may also bind with hydroxide ions present in the electrolyte solution to create the negatively charged edge of the nanopore. During operation of the device, an external pressure may be applied to one of the chambers such that a pressure gradient is formed, resulting in the asymmetrical  
15 passage of anions and cations through the nanopores from the chamber experiencing a higher pressure to the oppositely-disposed chamber having a lower pressure. For instance, a pore having a negatively charged surface or edge may be more selective toward cations, and which then allows a greater number of cations to pass through the membrane layer. This may in turn result in a streaming current i.e. generation of  
20 electricity. In so doing, mechanical energy may be advantageously converted to electrical energy.

The electrolyte may comprise an ionic liquid or an aqueous solution. The electrolyte may comprise one or more positively charged ions selected from  $H^+$ ,  $K^+$ ,  $Na^+$ ,  $NH_4^+$ ,  $Li^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{3+}$  or  $Al^{3+}$  and/or one or more anions selected from  $OH^-$ ,  
25  $Cl^-$ ,  $F^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $HCO_3^-$ ,  $HSO_3^-$ ,  $H_2PO_4^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $CH_3COO^-$ ,  $C_5H_9NO_4^-$ ,  $CO_3^{2-}$ ,

$\text{SO}_4^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  or  $\text{PO}_4^{3-}$ . In one embodiment, the electrolyte may be selected from Group 1 halide salts, e.g., KCl.

In one embodiment, the electrolyte is an ionic liquid. The ionic liquid may preferably have a melting point of below 100 °C, and is in a liquid state under ambient temperatures ranging from 15 – 35 °C. Non-limiting examples of ionic liquids may include imidazolium or pyridinium salts, such as hexafluorophosphate salts, tetrafluoroborate salts, or imide salts e.g. 1-butyl-2-methylimidazolium hexafluorophosphate ([BMIM]PF<sub>6</sub>). The electrolyte may also comprise a gel, ionomers such as nafion, or other polymeric matrix, provided that these liquids are electrically conductive or contain mobile, charged ions.

It has been found that the efficiency of the conversion of mechanical energy to electrical energy may be optimized by adjustment of one or more electrolyte parameters, including but not limited to the type of salt, salt concentration, and pH, in combination with one or more other variables such as membrane thickness, pore size, and the magnitude of the applied pressure gradient. In one embodiment, the molar concentration of the salt in the electrolyte may be provided in a range of from about 0.0001 to about 1 mol/L. More particularly, the salt concentration may be provided in ranges of from 0.001 to 0.01 mol/L, from 0.001 to 0.1 mol/L, from 0.01 to 0.1 mol/L, from 0.01 to 1 mol/L, or from 0.1 to 1 mol/L. In one embodiment a salt concentration of from 0.01 to 0.1 mol/L was advantageously found to provide optimized conversion yields of from 20 to 30% when combined with a 0.1M metal halide electrolyte and membrane pore size of around 3 nm in diameter, and wherein a pressure gradient of 3 bars was applied. Such a device was also able to provide a maximum output density of 2507 W/m<sup>2</sup>.

The concentration of the ions in the electrolyte may also be from 0.00005 M to 4 M (M being mol per dm<sup>3</sup>) such as about 0.0001 M, about 0.0005 M, about 0.001 M, about

0.005 M, about 0.01 M, about 0.05 M, about 0.1 M, about 0.5 M, about 1 M, about 2 M, about 3 M or about 4 M.

The ionic liquid or aqueous solution electrolyte may have a pH selected from 3 to 10.

The pH may be suitably adjusted in accordance with the material used for the porous

5 membrane and may depend on whether a positively or negatively charged membrane surface is operationally desirable. In one embodiment, the conductance and energy conversion efficiency of a porous membrane composed of 2D WS<sub>2</sub> in contact with a metal halide electrolyte was found to decrease as the electrolyte pH was adjusted from 3 to 5. However, the conductance and energy conversion efficiency was thereafter  
10 observed to improve as the electrolyte pH increased from 6 to 10. In one embodiment, optimal conductance and efficiency may be obtained at pH of from about 7 to 9, more particularly, from 8 to 9, and even more particularly, at pH 9. In another embodiment, optimal performance of 2D WS<sub>2</sub> membranes comprising nanopores of 2 to 30 nm in salt solutions of 0.001-0.1M LiCl was achieved at pH 9.

15 When the pH of the electrolyte is adjusted, the surface charge (and the surface charge density) of the porous membrane may be altered accordingly. Depending on the pH of the electrolyte, the surface charge on the porous membrane may be negative, positive or zero. At zero surface charge, the density of the negatively charged ions in the porous membrane may be balanced by the positively charged ions. The zero net  
20 charge may also be termed the isoelectric point.

The device may further comprise means for applying the pressure gradient across the membrane in order to actuate transport of the ionic species through the pore(s). In one embodiment, the means for applying said pressure may be a mechanical means. The means for applying the pressure gradient may also electrical or gravitational in nature.

25 In embodiments, the means for applying the pressure gradient may comprise a positive pressure source (e.g., pump) or a negative pressure source (e.g., a vacuum source),

wherein said means is coupled to at least one of the two chambers to thereby generate a pressure gradient across the porous membrane.

In another embodiment, the mechanical means may comprise an external compressive force configured to compress the volume of at least one chamber housing the electrolyte to thereby facilitate transport of the ions across the nanopores.

The pressure gradient between the at least two chambers above may also be formed by introducing an external pressure to one or both of the chambers. The pressure gradient formed may be in the range from 0.001 bar (or 1 mbar) to 20 bar such as 0.001 bar (1 mbar), 0.005 bar (5 mbar), 0.01 bar (10 mbar), 0.05 bar (50 mbar), 0.1 bar, 0.2 bar, 0.3 bar, 0.4 bar, 0.5 bar, 0.6 bar, 0.8 bar, 1 bar, 1.5 bar, 2 bar, 2.5 bar, 3 bar, 5 bar, 10 bar, 15 bar or 20 bar.

In another embodiment, the means may comprise an electrical source configured to apply an electrostatic force, e.g., a voltage or a potential difference, across the membrane to thereby drive the charged ions through the nanopores. The supplied voltage may be in the range of 1 mV (0.001 V) to 1000 mV (1 V) such as about 1 mV, about 5 mV, about 10 mV, about 20 mV, about 50 mV, about 100 mV, about 150 mV, about 200 mV, about 250 mV, about 300 mV, about 500 mV, about 750 mV or about 1000 mV.

Accordingly, the disclosed device may further comprise one or more electrodes. In one embodiment, each chamber may be respectively electronically communicated with one or more electrodes for applying a voltage across the membrane. The electrodes may also be used to detect the strength of the current generated by the passage of the ions through the nanopores. These electrodes may be further electronically coupled or connected to a sensor, a battery, a capacitor, or a load. Thus, the disclosed device may be capable of generating and/or storing electrical energy or may be used to supply

electrical energy directly to a load. Non-limiting examples of the electrodes may include but are not limited to Ag/AgCl, calomel, platinum, or carbon-based electrode. In a particular embodiment, the electrodes are Ag/AgCl electrodes.

The nanopore(s) may be formed by physical or chemical treatment of the membrane  
5 after it has been fabricated, e.g., via ions beam exposure, electron beam exposure, thermal annealing or chemical etching. The pore(s) may be formed as an integral part of the membrane's structure. For instance, the pores may be formed intrinsically during the synthesis of the membrane itself, e.g., by intentional introduction of defects in a self-assembly process for growing the 2D membrane. In one embodiment, the  
10 nanopore was formed by exposure of the 2D material to an electron beam from a transmission electron microscope (TEM).

The porous membrane may have a laminar structure of interlocked or cross-linked flakes of 2D material. The laminar structure or laminar organization above refers to structure or organization where the membranes are arranged or stacked in layers one  
15 upon another.

The nanopore(s) or nanosized-pore(s) may have a high surface charge at the edge of nanopore(s) or nanosized-pore(s). The presence of such surface charges may result in a high density of charged ions accumulating at the edges or openings of the nanopore channels. This may in turn result in the selectivity for oppositely charged ions present in  
20 the electrolyte that is in contact with the membrane surface.

The disclosed device may be advantageously scaled up and integrated with other components for various applications. The device may also be provided as a microfluidic or a nanofluidic device.

The disclosed device may be able to generate an output power density, which is  
25 calculated as the maximum power that an external load is able to harvest per nanopore

area. The output power density of the device may increase with the increase in the external pressure applied. A smaller pore size i.e. smaller pore diameter may result in an increase in the power density for the same external pressure applied. This may be due to smaller total area and higher ionic selectivity for smaller pore size. In  
5   embodiments of the disclosed device, this parameter may vary between 300 W/m<sup>2</sup> to 3000 W/m<sup>2</sup> such as about 300, about 500, about 1000, about 1500, about 2000, about 2500 or about 3000 W/m<sup>2</sup>.

The energy conversion efficiency of the device, as described herein, refers to the ratio of output electrical power to input mechanical power. The energy conversion efficiency  
10   may depend on the type of ionic species (including charges and size), concentration of the ionic species and pH of the liquid.

Depending on the factors like the dimensions of the nanopore(s), pH of the ionic solution and pressure gradient formed between the two chambers, the efficiency achieved in the porous membrane defined herein may be in the range of from about  
15   0.5% to about 30%, such as 0.5%, 1%, 2%, 5%, 8%, 10%, 12%, 15%, 18%, 20%, 21%, 22%, 23%, 24%, 25%, 26%, 27%, 28%, 29% or 30%. The efficiency may be any other values between the above ranges.

In one embodiment, a 2D nanopore device comprising WS<sub>2</sub> flakes having a 3nm nanopore immersed in a salt solution comprising 0.1 M LiCl at about pH 6  
20   advantageously achieved an efficiency of about 27.6 %.

In another embodiment, there is also provided a process for preparing a porous membrane having at least one layer of a 2D material, comprising the steps of: a) providing a 2D material; b) subjecting the 2D material to a treatment process selected from: exfoliation, ions beam exposure, electron beam exposure, thermal annealing

and/or chemical etching, to thereby form at least one nanopore extending through the thickness of the 2D material.

The porous membrane may further be incorporated on a substrate or a support material to form a substrate-supported membrane structure. The substrate or support  
5 may be a material that has high strength and fracture toughness such as silicon nitride ( $\text{SiN}_x$ ) or silicon oxide ( $\text{SiO}_2$ ). Other suitable substrates such as polymers (e.g. polystyrene and polyaniline) and alumina (including aluminium oxide or anodic aluminium oxide). The substrate or support material may act to improve the overall mechanical strength and fracture toughness of the porous membrane. In one  
10 embodiment, the porous membrane may be  $\text{WS}_2$  supported on silicon nitride or silicon oxide.

The step of providing a monolayer 2D material may comprise a physical vapor deposition or a chemical vapor deposition step. The 2D material may also be formed by exfoliation or micromechanical cleavage of a crystalline sample of said material. In  
15 an exemplary embodiment, the 2D material is  $\text{WS}_2$  which may be provided in the form of flakes.

Once the flake-like 2D material has been obtained, it may be transferred to a nanopore chip via a wet-transfer method, dry-transfer method or drop casted to form 2D material sheets. Thereafter, the sheets may be subjected to the electron beam exposure to form  
20 the nanopores. In a particular embodiment, the method for transferring the above 2D material is the wet-transfer method.

### **Brief Description of Drawings**

The accompanying drawings illustrate non-limiting embodiments of the invention and serve to explain the principles of the disclosed embodiments. It is to be

understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Figure 1a is a schematic diagram of an exemplary 2D nanopore mechanical energy harvester fabricated with two-dimensional (2D) membrane comprising a single nano-sized pore.

Figure 1b (left) is an optical micrograph of monolayer  $\text{WS}_2$  flakes prepared via chemical vapor deposition.

Figure 1c is an optical image (left) of  $\text{WS}_2$  flakes transferred to a nanopore chip comprising a membrane window using a wet transfer method and a micrograph (right) of a 6 nm nanopore drilled onto the  $\text{WS}_2$  sheet using an electron beam from a Transmission Electron Microscope (TEM).

Figure 1d is a Raman spectrum of the monolayer  $\text{WS}_2$  flakes prepared by chemical vapor deposition.

Figure 2 is a schematic diagram of an exemplary 2D nanopore mechanical energy harvesting device comprising an electrode and two fluidic chambers separated by a 2D membrane material comprising a nanopore.

Figure 3a is a schematic representation of an exemplary 2D nanopore mechanical energy harvester comprising two reservoirs filled with a salt solution and separated by a monolayer  $\text{WS}_2$  membrane, illustrated with a ball and stick drawings of the constituent atoms. The area bound by the dashed line was modelled for the COMSOL calculations of the 2D nanopore described herein.

Figure 3b is a graph plot showing the measured current and streaming potential of a 30 nm nanopore membrane in response to pressures being applied on the membrane.

Figure 4a is a graph plot showing the current and streaming potential response of the 2D nanopore membrane with (dashed line) and without (solid line) connecting with a load resistor.

Figure 4b is a graph plot showing the change in output power of the 2D nanopore membrane in response to a change in the load resistor

Figure 5a is a graph plot showing the variation in calculated maximum output power density of a 30 nm 2D nanopore membrane under different pressure gradients; and at salt concentrations ranging from 0.0001 M to 1M.

Figure 5b is a graph plot illustrating the relationship between maximum output power density and pressure gradients for membranes having 2D nanopores of diameters of 5 nm, 10 nm and 30 nm, respectively, using 1M KCl.

Figure 6a is a graph plot depicting the simulated and experimental relationships between streaming conductance and the concentration of the electrolyte using a membrane comprising a 2D nanopore of 11 nm in diameter and an applied pressure of 0.5 bar. Data points in the graph denote the experimental values of the streaming conductance while the solid lines represent the COMSOL simulation results of an 11 nm nanopore with  $-400 \text{ mC/m}^2$  edge surface charge and a 11nm nano-channel ( $1\mu\text{m}$  in length) with  $-50 \text{ mC/m}^2$  surface charge (silica).

Figures 6b and 6c illustrate the COMSOL calculated profile for a 11 nm 2D nanopore in 0.01M KCl and 0.1 M KCl respectively, where the arrows indicate the fluid velocity and the color plot indicates the space charge density in  $\text{mol/m}^3$ , The plot extending across the cross section represents the normalized current density within the pore; while the circular line indicates the equipotential lines outside the charged edges.

Figures 7a and 7b are graph plots demonstrating the response of conductance and streaming conductance as the concentration of the KCl salt solution is increased.

Figure 8a is a graph plot showing the estimated efficiency and output power density of a 2D WS<sub>2</sub> membrane comprising a nanopore of 11 nm (top), 4 nm (middle) and 2 nm (bottom) at different concentrations of KCl.

Figure 8b is a graph plot showing the maximum efficiency as a function of nanopore diameter at optimal working concentrations.

Figure 8c is a graph plot showing the optimal Debye length for efficiency as a function of nanopore diameter.

Figure 9a is a graph plot illustrating the response of the streaming conductance and conductance to changes in pH of the salt solution.

Figure 9b is a graph plot demonstrating the change in theoretical efficiency of the nanopore membrane as the pH of the KCl salt solution increases.

Figure 10a is a graph plot showing efficiency of a WS<sub>2</sub> membrane comprising a 11 nm 2D nanopore under different concentrations of LiCl, NaCl and KCl salt solutions

Figure 10b is a graph plot showing the changes in the calculated theoretical efficiency of a 2D WS<sub>2</sub> membrane comprising a 4 nm nanopore at 1 bar pressure gradient as the cationic mobility for various combinations of cations and anions is varied.

Figure 11 is a comparison of the calculated theoretical efficiency and maximum power output density of the 2D nanopores as described herein with other nanoporous membrane, nanochannels, microchannels, MEMS piezoelectric and nanopores which are known in the art. Data points in the graph denote the maximum output power density and theoretical efficiency of a nanostructured device at an optimal salt concentration. The corresponding pore size, where applicable, is provided next to each data point.

Figure 12 is a graph plot which shows the efficiency of a 2D WS<sub>2</sub> membrane comprising a 3 nm nanopore a 0.1M salt solution under a pressure gradient of 3 nm.

### Examples

- 5 Non-limiting examples of the invention and a comparative example will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

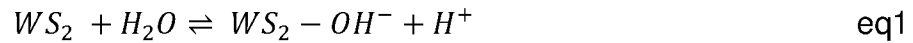
#### Example 1 – Fabrication of 2D nanopore chip

Tungsten sulfide (WS<sub>2</sub>) monolayer materials were prepared from tungsten oxide and sulfur via chemical vapor deposition methods. Monolayer WS<sub>2</sub> flakes were grown by  
10 reacting tungsten oxide and sulfur in Argon under a flow rate of 200 sccm at a temperature of 1100°C for about 10-20 minutes. The WS<sub>2</sub> flakes which are formed on the silicon substrate are shown in Figure 1b. The monolayer WS<sub>2</sub> flakes were distinguished by the color of the flakes and Raman spectroscopy was used to confirm  
15 the formation of the monolayer WS<sub>2</sub> flakes (Figure 1d). The WS<sub>2</sub> monolayer flakes were transferred to a nanopore chip by wet-transfer methods. Figure 1a is schematic diagram of an exemplary nanopore chip; while Figure 1c is an optical image of the nanopore chip. The nanochip was prepared with a silicon frame and a silicon nitride membrane window. A hole was drilled onto the silicon nitride membrane window which  
20 was then covered by the monolayer WS<sub>2</sub> flake. A single nanosized pore was drilled on the monolayer WS<sub>2</sub> by the electron beam of a transmission electron microscope (TEM).

#### Example 2 – Finite element calculation of 2D nanopore

The fabrication of a nanopore within the WS<sub>2</sub> monolayer is believed to cause the covalent bonds of WS<sub>2</sub> to be severed, thereby exposing unpaired S atoms, which lead  
25 to negatively charged nanopore edge. Furthermore, it is hypothesized that the WS<sub>2</sub> surface can bind with hydroxide ions in a solution contributing to a negatively charged

nanopore. The binding of the hydroxide ions in solution to the  $WS_2$  surface is represented in equation 1



The mechanism of energy conversion is therefore believed to be as follows. When pressure is applied onto the reservoir on one side, an uneven number of ions will pass through the nanopore in the direction of the pressure-driven flow due to the selectivity of the region close to negatively charged surface of the nanopore, creating streaming current.

The properties of the pressure driven energy generation were also studied using a finite element calculation of 2D nanopore based on the geometry of fig. 3(a) using COMSOL was also carried out. The model employs two different surface charge conditions, one with high surface charge at the edge of the pore  $\sigma_e$ , and one on the membrane plane  $\sigma_p$ .

A COMSOL Multiphysics 5.1 platform was used for the calculations. The model imposed azimuthal symmetry for simplification and consisted of two quadrants of circles connected by an aperture as shown in Figure 3a. All contributions from the fluidic chamber were neglected, and the silicon chip cavity, as we assumed a region considerably far enough (around  $0.5 \mu\text{m}$ ) from the pore, has the similar potential as the electrode. The model employs two different surface charge conditions, one with high magnitude at the edge of the pore, and one on the membrane plane.

The calculation is simplified by using ordinary Poisson-Nernst-Planck approach. The physical constants are fixed to be constant through all concentration. The model solved coupled equations in stationary and time-independent manner. The equation includes a Stokes equation, Poisson equations and two Nernst equations in chemical potential format coupling together.

$$-\vec{\nabla}p + \mu \nabla^2 \vec{u} - e N_A \rho_e \vec{\nabla}V = 0$$

$$\nabla^2 V = -\frac{\rho_e}{\varepsilon} = -\frac{e}{\varepsilon} \sum_i z_i C_i$$

$$-\vec{\nabla} \cdot \vec{J}_i = \nabla^2 \mu_i = 0, \mu_i = kT \ln C_i + z_i e V$$

- 5 The boundary conditions are chosen as follows: at the membrane surface,

$$\vec{n} \cdot \vec{\nabla} \mu_i = 0,$$

$$\varepsilon \vec{n} \cdot \vec{\nabla} V = -\sigma,$$

an equipotential border,

$$\mu_i = \text{Const.},$$

$$10 \quad V = \text{Const.},$$

$$p = \text{Const.},$$

For each condition of concentration, voltage and pressure, electrical current and flow rate is extracted,

$$I = \sum_i z_i \int d\vec{A} \cdot (-\gamma_i C_i \vec{\nabla} \mu_i + C_i \vec{u})$$

$$15 \quad Q = \int d\vec{A} \cdot \vec{u}$$

### Example 3 – Fabrication of 2D nanopore mechanical energy harvester

The nanopore chip prepared according to the methods of Example 1 was inserted into a fluidic cell comprising a salt solution. The salt solution may comprise KCl, NaCl and  
 20 LiCl at concentrations of 0.1 mM to 1M. These salt solutions were filtered with rapid flow filter units before use. A silver/silver chloride (Ag/AgCl) electrode was connected to the *cis* and *trans* chamber to apply potential and measure the generated current. An exemplary fluidic cell comprising two liquid-filled chambers separated by a monolayer WS<sub>2</sub> membrane on the nanopore chip is illustrated in Figures 2 and 3a.

High purity nitrogen gas was used to apply pressure to the fluidic cell and a gas regulator was used to control the gas pressure applied to the fluidic cell. A Capacitor Feedback Patch Clamp (Axopatch 200B-2) and Data Acquisition System (Digidata 1550B1) was used to collect data regarding the performance of the nanopore device.

#### 5 **Example 4 - Pressure driven energy conversion performance**

The performance of the nanopore energy harvester in the conversion of mechanical energy to electrical energy was evaluated by performing a pressure driven energy conversion experiment. A pressure was applied across the nanopore and the resultant current-voltage response (I-V response) of the nanopore under pressure was measured using the Capacitor Feedback Patch Clamp (Axopatch 200B-2) and Data Acquisition System (Digidata 1550B1) attached to the 2D nanopore mechanical energy harvester as described in Example 3. Figure 3b is a graph of the I-V response of a 30 nm 2D nanopore to pressure.

From the IV response curve, the short circuit current  $I_{sc}$  ( $V=0$ ) and open circuit voltage  $V_{oc}$  ( $I=0$ ) with and without applied pressure were obtained and the short-circuit streaming current ( $I_{str}$ ) and open-circuit streaming voltage ( $U_{str}$ ) from open-circuit voltage of the nanopore device were calculated as below:

$$I_{str} = I_{sc} (\text{with pressure}) - I_{sc} (\text{without pressure})$$

$$U_{str} = V_{oc} (\text{with pressure}) - V_{oc} (\text{without pressure})$$

Without pressure gradient, no current or potential is generated. When a pressure of 0.5 bar was applied across the nanopore from the *cis* chamber to *trans* chamber, an I-V curve which is left shifted from the origin was observed, indicating that positive  $I_{str}$  and  $U_{str}$  were generated. On the contrary, when pressure was applied from the *trans* chamber to *cis* chamber, the I-V curve demonstrated a right shift. In this instance, a negative  $I_{str}$  and  $U_{str}$  was obtained. This suggests that the  $WS_2$  nanopore comprises a

negatively charged edge, as positive ions are the dominant species which are pass through the stream.

With increasing pressure gradient of 0.5 bar to 3 bar and applied voltage within 1000 mV range, the I-V curves demonstrated a linear increase in current and voltage depending on the streaming direction, indicating a stable output electrical energy in response to an applied pressure. The nanopore device demonstrated an almost symmetrical response in both directions to pressure and voltage applied. In addition, the slope of the I-V response curves, which is representative of the nanopore conductance, remained the same with no significant coupling or bias between two driving forces. This implies that the size of nanopore and its charge selective zone are not significantly altered by the applied pressure.

#### **Example 5 - Maximum output power density**

The performance of the 2D nanopore may be evaluated by determining its maximum output power density. Maximum output power density is defined as the highest power that an external load can harvest per nanopore area. Within the linear response regime, maximum output power is believed to be one fourth of the product of  $U_{str}$  and  $I_{str}$ . The maximum output power density of the nanopore energy harvester was evaluated as below. To verify this, load resistors were connected to the fabricated nanopore energy harvester and the resistor was powered.

The I-V response and output power of the nanopore energy harvester were measured and these are shown in Figures 4a and 4b, respectively. Figure 4a demonstrates the I-V response of the nanopore connected to a load resistor (dashed line) and without connecting with a load resistor (solid line) when different pressure gradients are applied; while Figure 4b shows the output power of the nanopore in response to changes in the resistance of the load resistor.

As above, the maximum output power by an optimal load resistance is believed to be one fourth of the product of  $U_{str}$  and  $I_{str}$  in linear I-V curve. Any related output power density recited herein is also considered to be with reference to an optimal load resistance.

- 5 Based on this relationship, the maximum output power density for each nanopore may be calculated using equation 2 below, wherein,  $r$  is the radius of the nanopore.

$$P.D._{max} = \frac{I_{str}U_{str}/4}{\pi r^2} \quad \text{eq(2),}$$

The calculated output power density of a 30 nm nanopore under different pressure gradient and concentration is shown in Figure 5a. At concentrations of 1mM to 1M KCl,  
10 output power density shows a quadratic response to an increase in pressure; and is proportional to the input hydraulic power ( $P_{in}=pQ$ ).

Figure 5b shows that output power density also demonstrates a quadratic response to an increase in applied pressure for 5, 10, 30 nm nanopores in a salt solution of 1M KCl. Figure 5b shows that smaller pores may result in higher output power density. This is  
15 believed to be a result of a smaller total area and higher ion selectivity of small pores.

### Example 6. Energy Conversion Efficiency

Another key performance indicator for the nanopore, energy conversion efficiency, is defined as the ratio of output electrical power to input mechanical power as shown in equation 3 below.

$$\varepsilon_{max} = \frac{P_{max}}{P_{in}} \quad \text{eq(3)}$$

As discussed, the maximum output power,  $P_{max}$  is one fourth of the product of  $I_{str}$  and  $U_{str}$ . For input hydraulic power ( $P_{in} = pQ$ ), a Sampson flow model is chosen regarding the geometry of access from bulk to circle cross-section. Therefore,  $\varepsilon_{max}$  can be

estimated according to equation 4 below wherein  $\eta$  is the viscosity,  $r$  is nanopore radius and  $L$  is the membrane thickness.

$$\varepsilon_{max} = \left( \frac{I_{str}^2 R_{pore}}{4} \right) \left( \frac{P^2 \pi r^4}{(3\pi r + 8L)\eta} \right)^{-1} \quad \text{eq(4)}$$

To determine the factors which affect  $\varepsilon_{max}$ , the equation above may be expressed to be proportional to the conductance  $S_{str}$ , nanopore resistance  $R_{pore}$  and hydraulic resistance  $Z$ . This is also consistent with other pressure driven energy conversion studies, where the product of  $S_{str}^2 R_{pore} Z$  is usually named as figure of merit ( $\alpha$ ) of energy conversion efficiency. As nanopore electrical resistance  $R_{pore}$  is inversely proportional to solution conductivity, while streaming conductance  $S_{str}$  is strongly related to space charge distribution which is primarily governed by the pore surface charge, the overall maximum efficiency  $\varepsilon_{max}$  may be described to be dependent on the ionic species, ion concentrations and pH conditions.

The  $I_{str}$  of a 11 nm 2D nanopore was measured at various salt concentrations and the concentration dependence of streaming conductance for an 11nm nanopore is shown in Figure 6a. Data points shown in Figure 6a represent the measured response of the streaming current to pressure at different concentrations of KCl, under a pressure of 0.5 bar, while the solid line is a COMSOL simulation result of a 11 nm 2D nanopore having a surface charge of -400 mC/m<sup>2</sup> on the pore edges and -50 mC/m<sup>2</sup> on the surface. Both the simulated result and experimental measurement show that the streaming conductance increases as the concentration of the salt solution increases.

This is in contrast from corresponding energy harvester devices which utilize micro- and nano-channels. As illustrated in Figure 6a, a COMSOL simulation of an 11 nm nanochannel with -400 mC/m<sup>2</sup> and -50 mC/m<sup>2</sup> surface charge shows that the streaming current decreases as the concentration of the salt solution increases. This is thought to

be due to the localized edge surface charge effects and concentration dependent current distribution within the 2D nanopore which may be referred to as “Edge focusing effects”. Such effects are further described in figures 6b and 6c.

Figures 6b and 6c illustrate a COMSOL-calculated profile of a nanopore in the presence of 0.01M KCl and 0.1M KCl salt solution, respectively. In figures 6b and 6c, the arrows represent the fluid velocity profile through a nanopore, while the colour plot represents the space charge density of ions at different KCl concentrations under the condition of applied pressure with zero voltage. Along the cross-section, normalized current density profiles and circular lines showing the equipotential lines outside the charged edges are also shown. From Figures 6b and 6c, it may be seen that at a concentration of 0.1 M KCl (Figure 6c), the volume charge density is localized closer to the pore edge as compared to the lower concentration of 0.01 M KCl (Figure 6b).

Since fluid velocity generated by pressure gradient is maximized within the pore cross-section in axial direction, more streaming current is generated as more space charge density is localized closer to the pore plane. The current density plot clearly shows the difference in magnitude between nanopores in the different salt concentrations and demonstrates the effect of salt concentration on the streaming current and conductance.

In contrast with the 2D nanopores, in the uniform nanochannel geometry, fluid velocity gradient is more prominent in the cross-sectional direction, causing the space charge to be localized closer to the wall at high concentration, resulting in a lower streaming current. The difference in trend may be attributed to the difference geometry between the nanochannel and nanopore. While it is possible that the relaxation of space charge in 2D nanopores may induce a reverse current that mitigates the performance of the streaming current by a partial factor, the overall power generated using 2D nanopores is comparatively larger.

Streaming conductance  $S_{\text{str}}$  was also measured for the 2D nanopore mechanical energy harvester comprising a 2D nanopore of 2 nm, 4 nm, 11 nm and 30 nm in different salt solutions. As shown in Figures 7a and 7b, streaming conductance  $S_{\text{str}}$  increases in response to an increase in concentration, while nanopore resistance  $R$  continually decreases as with an increase in the concentration of the salt solution.

Considering the strength of the additional hydraulic resistance  $Z$  from induced electrical forces is negligible and the effect of salt concentration on streaming conductance and nanopore resistance described above, the dependency of the energy efficiency of a 2D nanopore on the concentration of the salt solution may be studied. A plot of the experimental data of energy efficiency and output power density against salt concentration (Figure 8a) shows that energy efficiency and power density reaches a peak at a specific concentrations, for a specific pore size. In addition, it is observed that peak conditions shift to higher salt concentrations as the size of the 2D nanopore decreases. Figure 8b also shows that at optimal salt concentrations, 2D nanopores of smaller sizes demonstrate higher energy efficiency.

The shifting of the optimal efficiency and power density according to the concentration of the salt solution suggests that an optimal Debye length/nanopore size ratio may contribute to the optimal efficiency of the 2D nanopore. Debye length is commonly known to be an indication of the length of a non-electroneutral region at a specific salt concentration. From the energy efficiency of the 2D nanopores, the optimal Debye length, may be calculated according to equation 5 below, where  $C$  is the salt concentration,  $\varepsilon$  is the solvent electrical permittivity,  $T$  is the temperature,  $e$  is electron charge and  $k_B$  is Boltzmann constant.

$$\lambda_D \equiv \sqrt{\varepsilon k_B T / e^2 C} \quad \text{eq(5)}$$

A plot of the optimal Debye length as a function of nanopore diameter is shown in Figure 8c. From this plot, the observed optimized Debye length/nanopore diameter ratio is about 0.4.

#### **Example 7 – Effect of pH on energy efficiency**

5 Based on the proposed mechanism of energy conversion discussed above, it is hypothesized that the binding of hydroxide ions on the membrane promotes surface charge of the nanopore which allows selectivity towards ions in the solution. The effect of the hydroxide ion concentration on the efficiency of the 2D nanopore membrane was therefore studied by measuring and calculating the power density and energy  
10 conversion efficiency of a membrane comprising a nanopore of 11 nm in 0.01M KCl salt solutions of varying pH at a pressure gradient of 0.5 bar. The pH of the salt solutions was adjusted using solutions of 0.01M HCl and 0.01M KOH.

A plot of the conductance and streaming conductance of the 2D nanopore in solutions of varying pH is provided in Figure 9a. From Figure 9a, at a pH of 3, it is believed that  
15 the net charge of the nanopore is positive, and only a low conductance is observed. As the nanopore approaches pH 5, the conductance decreases, indicating that the surface charge of the nanopore is approaching its isoelectric point. As the pH increases further and the concentration of hydroxide ions increases, the streaming conductance also demonstrated an upward trend.

20 A plot of the efficiency of the 2D nanopore at different pH (Figure 9b) shows that maximum efficiency is achieved at pH 9.

#### **Example 8 – Effect of ionic species on energy conversion efficiency**

The effect of the conductivity of various ionic species in the salt solution on the performance of the 2D nanopore was studied by preparing solutions of common salts  
25 such as KCl, NaCl and LiCl at concentrations of 0.3M. The efficiency of a 2D nanopore of 11 nm under a pressure gradient of 1 bar was calculated as shown in Figure 10a.

Based on Figure 10a, it was observed that highest efficiency was achieved when salt solutions based on lithium chloride were utilized.

As the energy conversion efficiency is dependent on the passage of ionic species through the nanopore, it is hypothesized that mobility of the ionic species contributes to mobility of the ions through the nanopore. As such, numerical COMSOL calculations on the cation mobility were carried out and a plot of the efficiency against ion mobility for a nanopore having a surface charge of  $-0.5 \text{ C/m}^2$  in salt solutions of 0.3M under a pressure gradient of 1 bar is shown in Figure 10b. As can be observed from the calculations, the efficiency of the 2D nanopore improves from KCl to LiCl with fixed anion mobility. Based on the calculations carried out for large anionic species such as  $\text{C}_5\text{H}_9\text{NO}_4^-$ , the performance of the 2D nanopore may be further optimized by selecting salts comprising low mobility cations and large organic anions.

#### **Example 9 – Optimizing performance of 2D nanopore**

Based on examples 6-8, it was observed that pore size, salt solution concentration, ionic species and pH may be optimized to achieve high efficiency of the 2D nanopore mechanical energy harvester. The highest efficiency achieved for the 2D nanopore described herein was 27.6 % when a 3 nm nanopore on  $\text{WS}_2$  flakes was used in a salt solution comprising 0.1M LiCl at pH 6 under a pressure gradient of 3 bar. This is illustrated in Figure 12. The maximum output power density obtained under these working conditions was  $2507 \text{ W/m}^2$  when a pressure gradient of 3 bar was applied.

#### **Comparative example**

The performance of the nanopore device described herein was compared with other nanoporous membranes, nanochannels, microchannels, MEMS piezoelectric devices and other nanopores known in the art. Calculations of the output power density of each nanopore was carried out using 3 bar as the input pressure. The calculated efficiency and maximum output power density for each of these devices are provided on Figure

11. The parameters of the various devices used for the comparison are as described below:

Microchannels : gold coated glass microchannel array with a pore diameter of 10  $\mu\text{m}$

Nanochannels : height of 75 nm, width of 50  $\mu\text{m}$  and length of 4.5 mm

5 Nanopore : polyethylene terephthalate nanopore having inner radius of 31 nm, open radius of 120 nm

Nanoporous membrane : Nafion membrane having pores of 25 to 1000 nm with a length of 201  $\mu\text{m}$

As can be observed, the 2D nanopores described herein demonstrated high output  
10 power as compared to other devices in the art. In addition, 2D nanopores having a diameter of 2-3 nm are able to achieve both high output power and energy conversion efficiency as compared to other devices known in the art.

### **Industrial Applicability**

The device for generating electrical current as described herein may be used for  
15 the harvesting of mechanical energy from the environment for the generation of electrical energy. Mechanical energy powered by natural phenomena such as winds and tides may be harvested using such devices and this provides for a clean and renewable way to generate power. In addition, its ease of manufacture enables industrial scale up of such devices for the assembly of power generators.

20

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the  
25 appended claims.

**Claims**

1. A device for generating a current, comprising:
  - i. at least two chambers partitioned by a membrane, each chamber housing an electrolyte; the membrane being a two-dimensional (2D) membrane and comprising at least one nano-sized pore permitting the passage of at least one ionic species contained in said electrolyte across the membrane; and
  - ii. means for applying a pressure gradient to at least one of the chambers, for transporting said ionic species across the membrane, wherein the transport of said ionic species generates a current.
2. The device according to claim 1, wherein said membrane is a monolayer membrane or a multi-layer membrane having a thickness of less than 20 nm.
3. The device according to claim 1, wherein said pore comprises a pore diameter of from 2 nm to 50 nm.
4. The device according to claim 1, wherein the membrane comprises a positively charged or negatively charged surface.
5. The device according to claim 1, wherein the membrane comprises a material selected from the group consisting of: graphene, hexagonal boron nitride, transition metal dichalcogenides ("TMD"), covalent organic frameworks, M-xenes (with M being a transition metal), clays and metal-organic frameworks.
6. The device according to claim 1, wherein said membrane comprises a monolayer tungsten disulfide ( $WS_2$ ) or substantially 2D  $WS_2$ .

7. The device according to claim 1, wherein the electrolyte comprises an ionic liquid or an aqueous solution.
8. The device of claim 1, wherein said electrolyte comprises one or more positively charged ions selected from  $H^+$ ,  $K^+$ ,  $Na^+$ , or  $Li^+$ .
9. The device according to claim 1, wherein the electrolyte comprises one or more anions selected from  $OH^-$ ,  $Cl^-$ ,  $F^-$ ,  $HCO_3^-$ , or  $C_5H_9NO_4^-$ .
10. The device according to claim 1, wherein said electrolyte is an ionic liquid.
11. The device according to claim 1, wherein the electrolyte has a molar concentration in the range of from 0.0001 to 0.1 mol/L.
12. The device according to claim 1, wherein the ionic liquid or aqueous solution has a pH selected from 3 to 10.
13. The device according to claim 1, wherein said means for applying the pressure gradient is a mechanical means.
14. The device according to claim 13, wherein said mechanical means is a pump, a vacuum source, or a positive pressure source.
15. The device according to claim 1, wherein each chamber is respectively electronically communicated with one or more electrodes for applying a voltage across the membrane.

16. The device according to claim 15, wherein said electrodes are connected to a sensor, a battery, a capacitor, or a load.
17. The device according to claim 1, wherein the pore is formed on said membrane by a process selected from electron-beam treatment, ion beam treatment, laser etching, or chemical etching.

Figure 1a

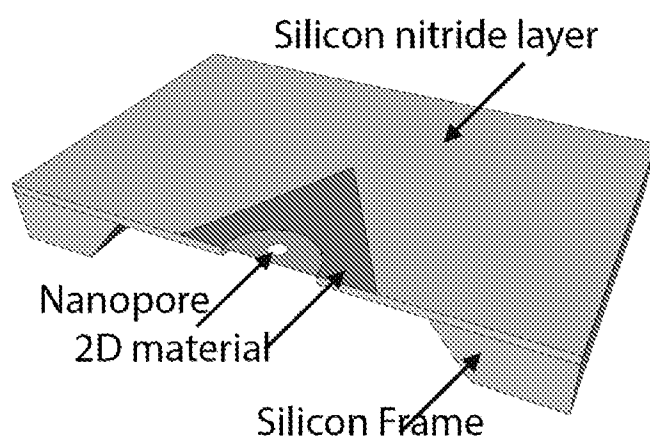


Figure 1b

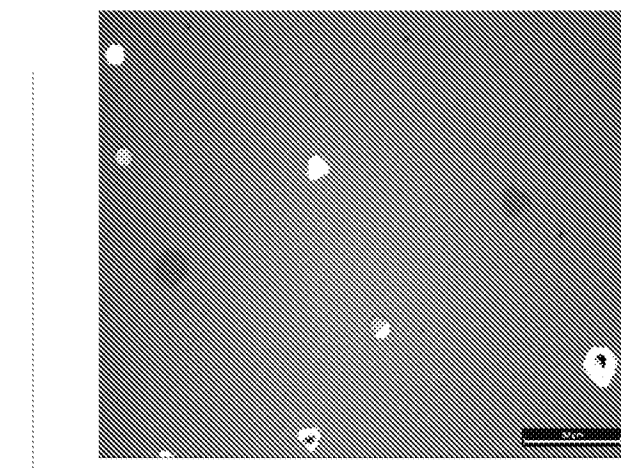


Figure 1c

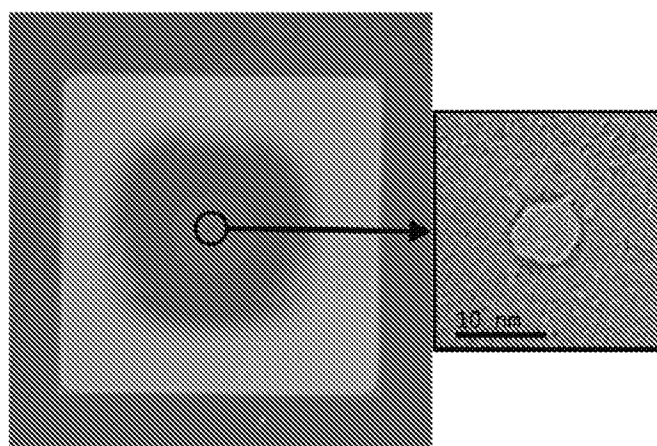


Figure 1d

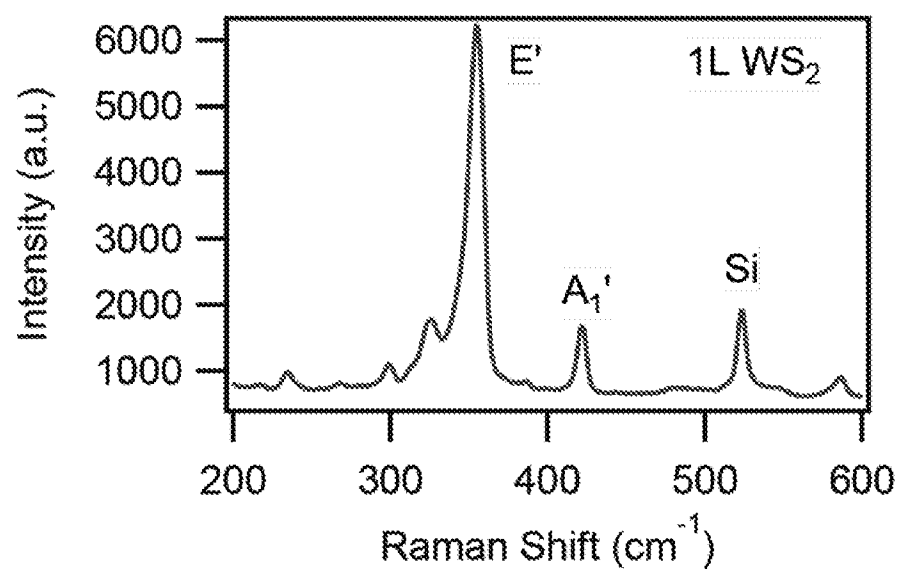


Figure 2

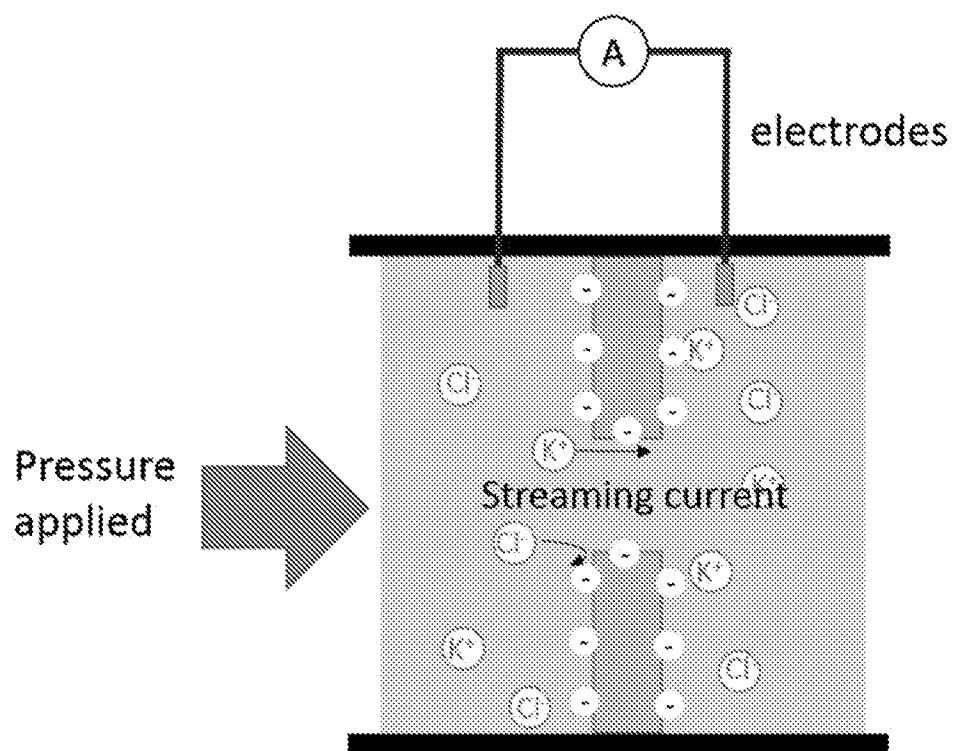


Figure 3a

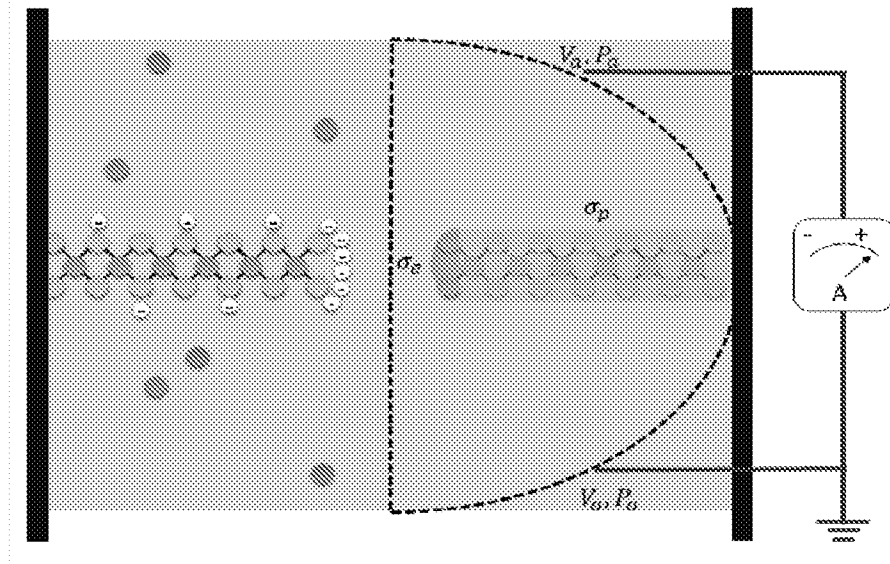


Figure 3b

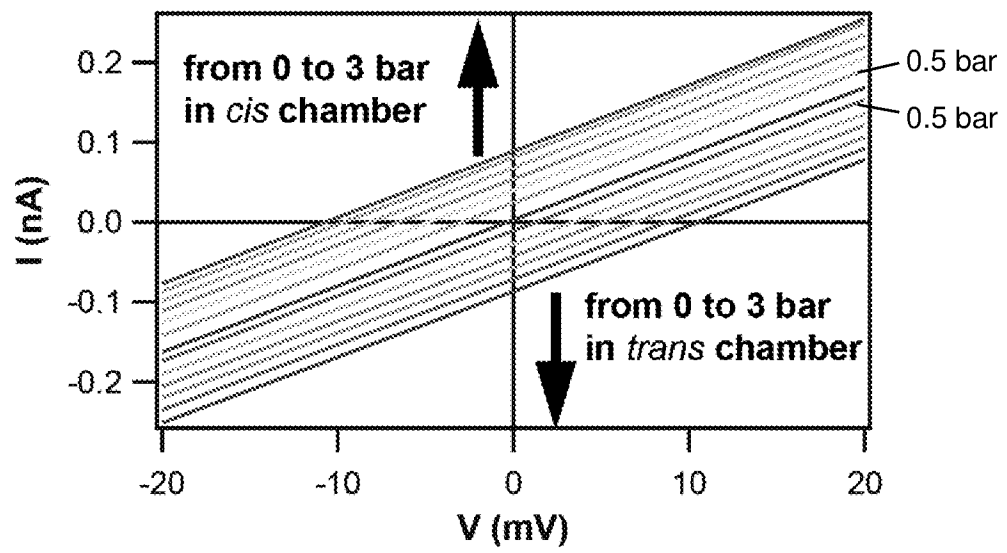


Figure 4a

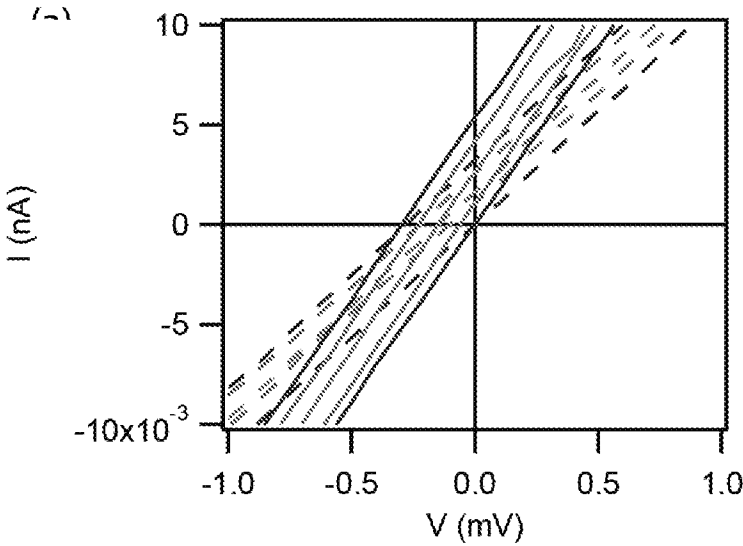


Figure 4b

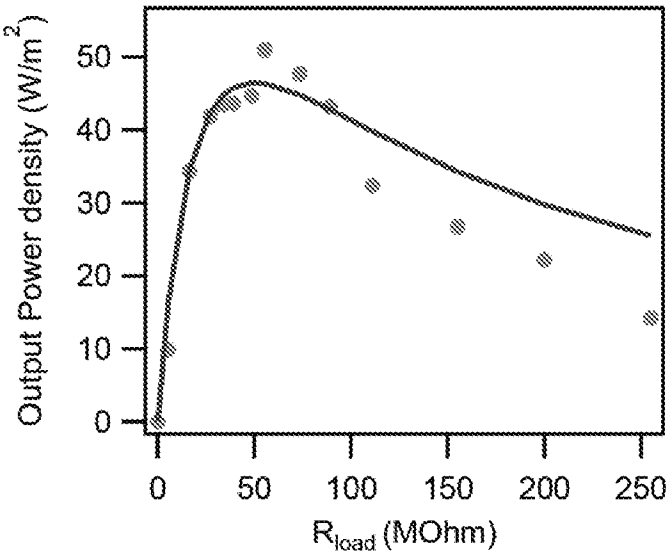


Figure 5a

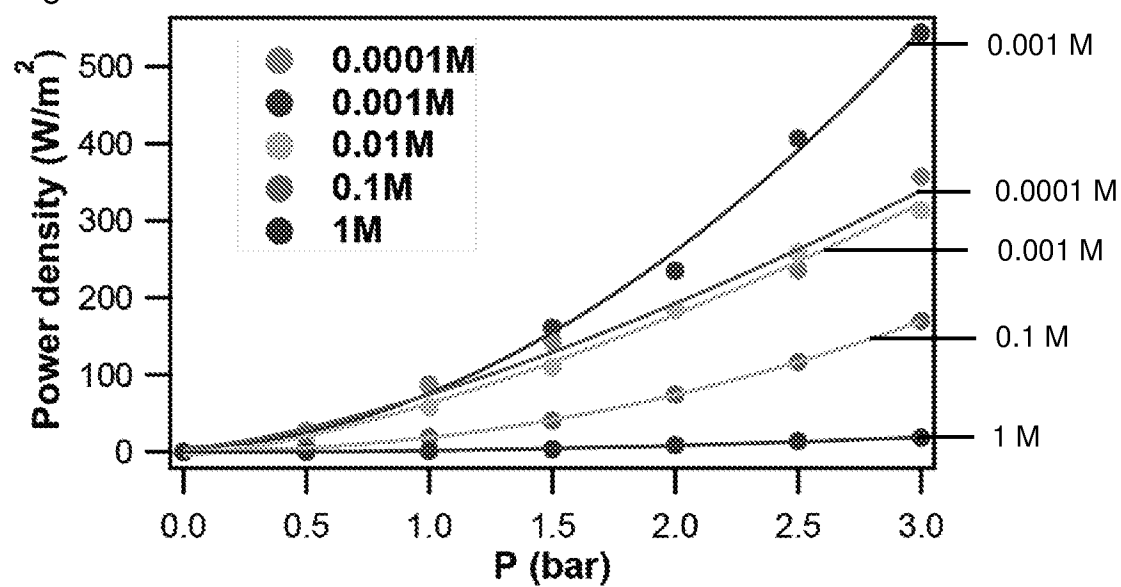


Figure 5b

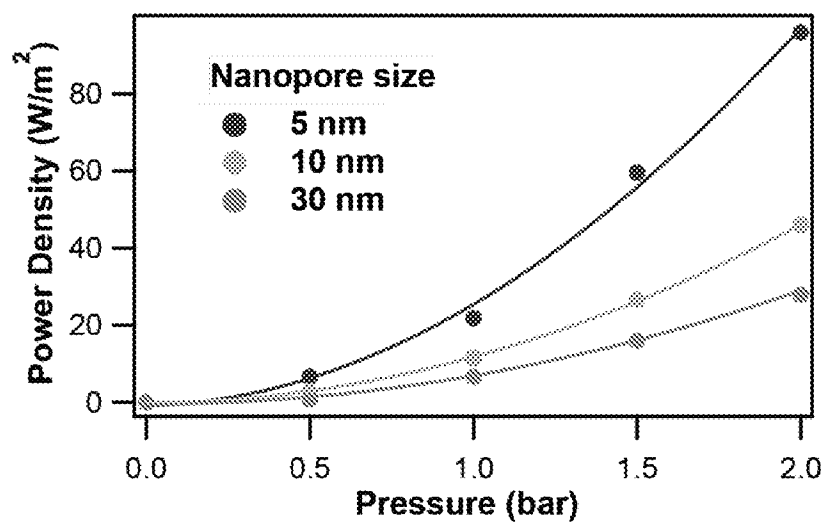


Figure 6a

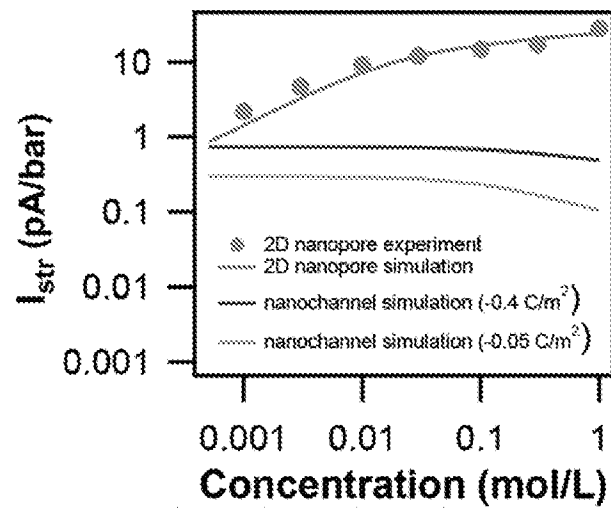


Figure 6b

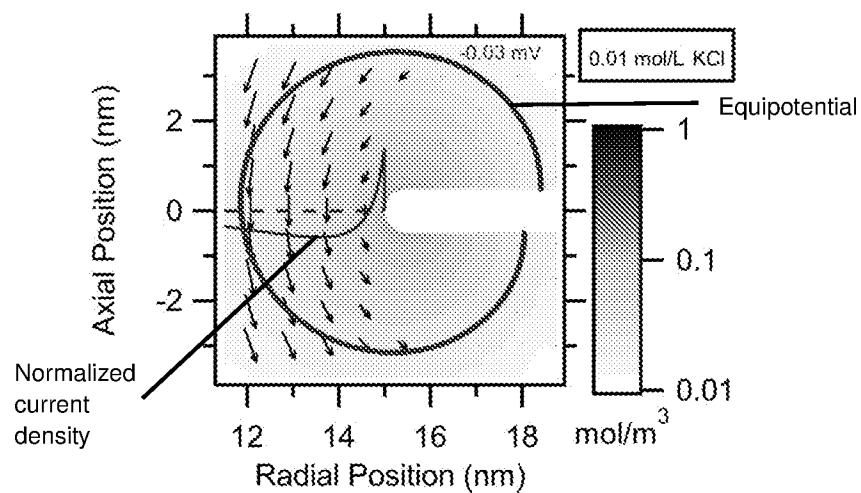


Figure 6c

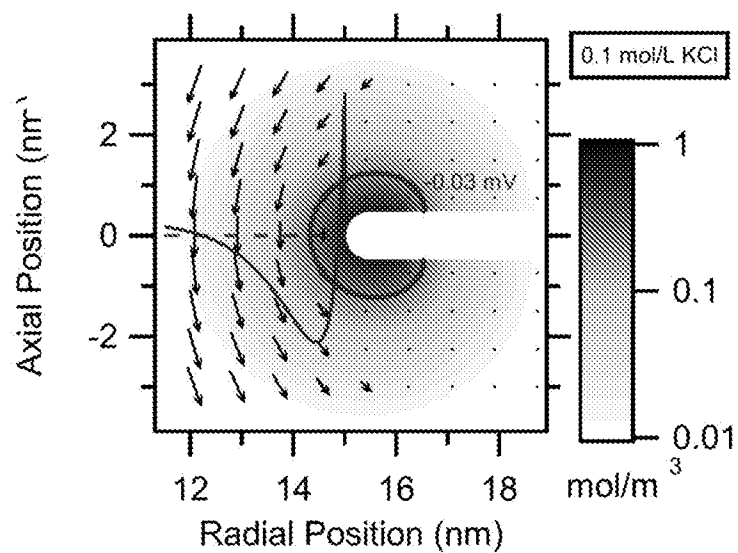


Figure 7a

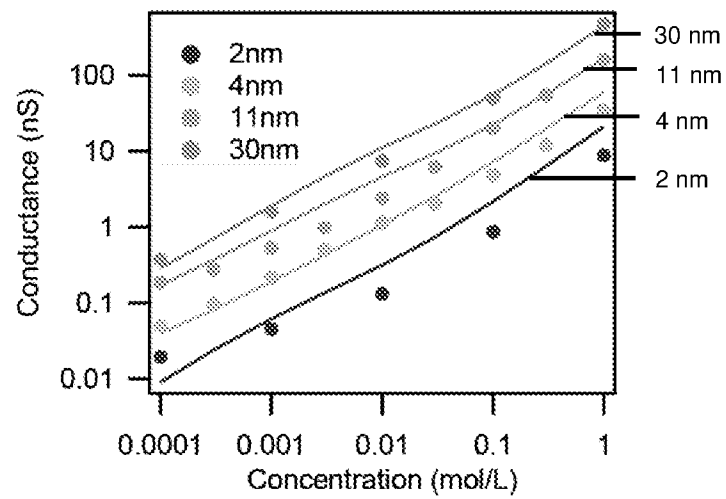


Figure 7b

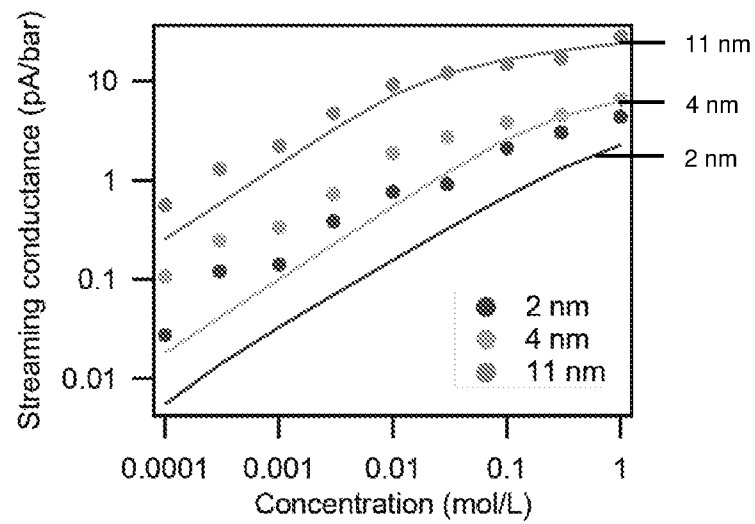


Figure 8a

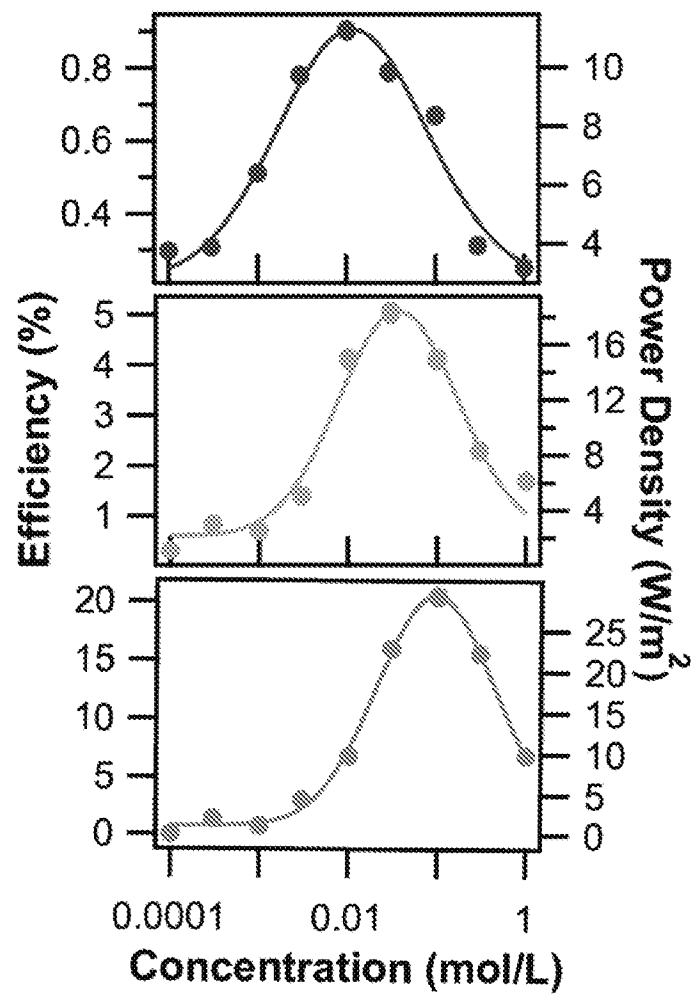


Figure 8b

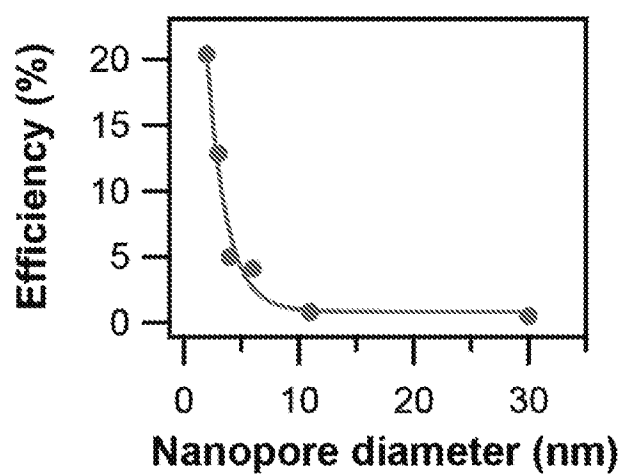


Figure 8c

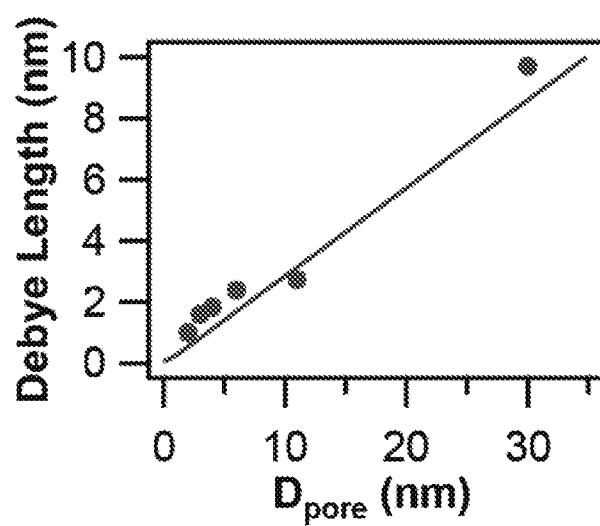


Figure 9a

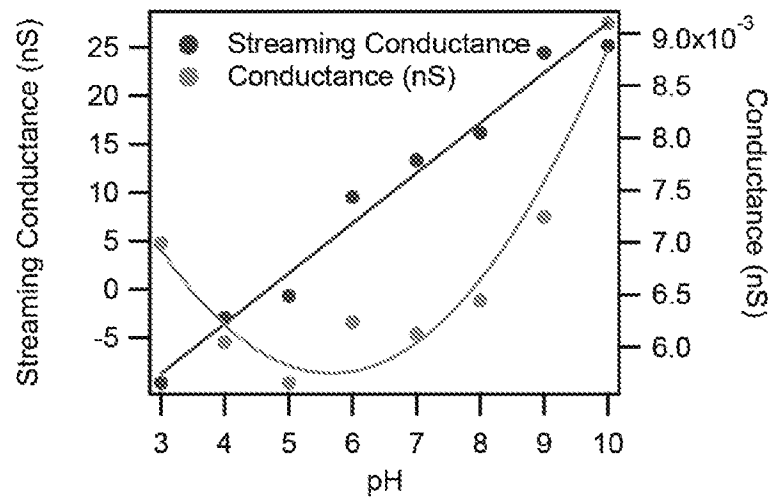


Figure 9b

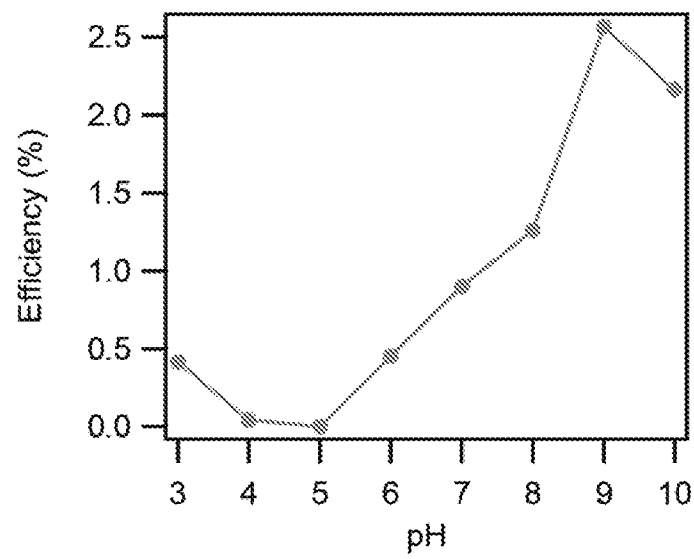


Figure 10a

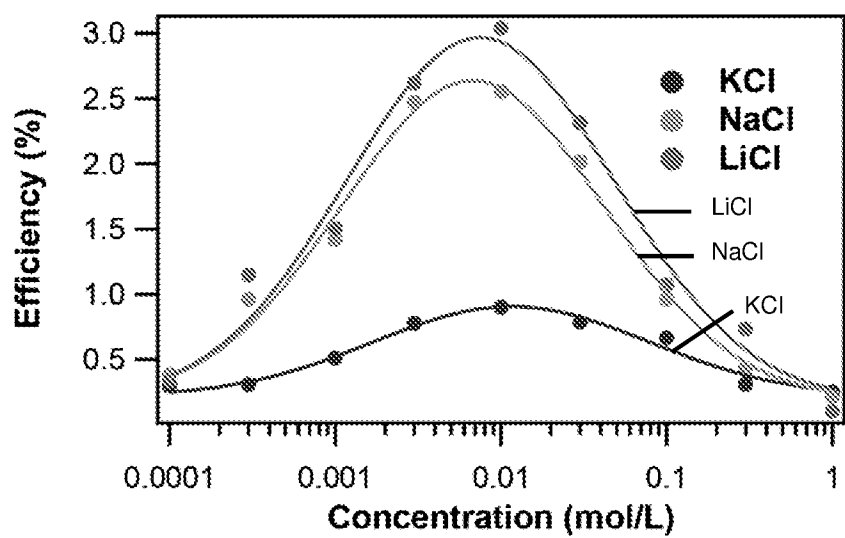


Figure 10b

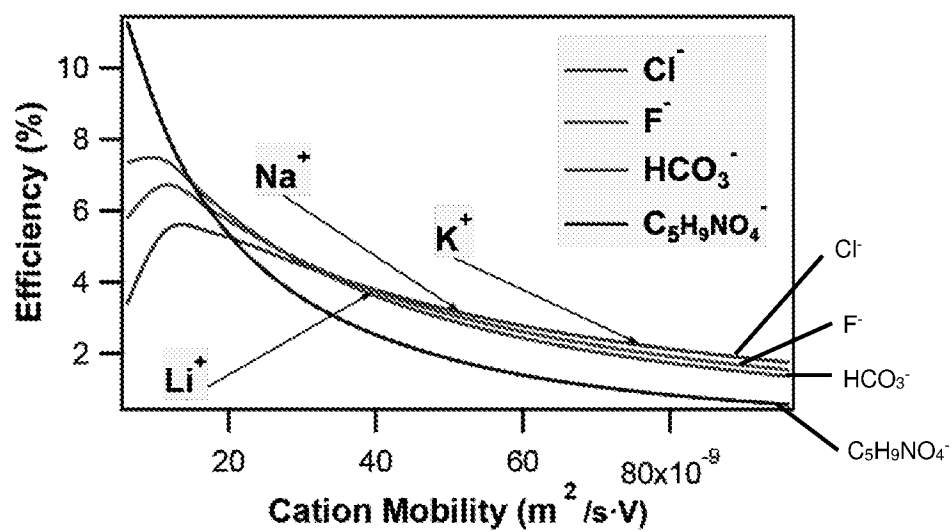


Figure 11

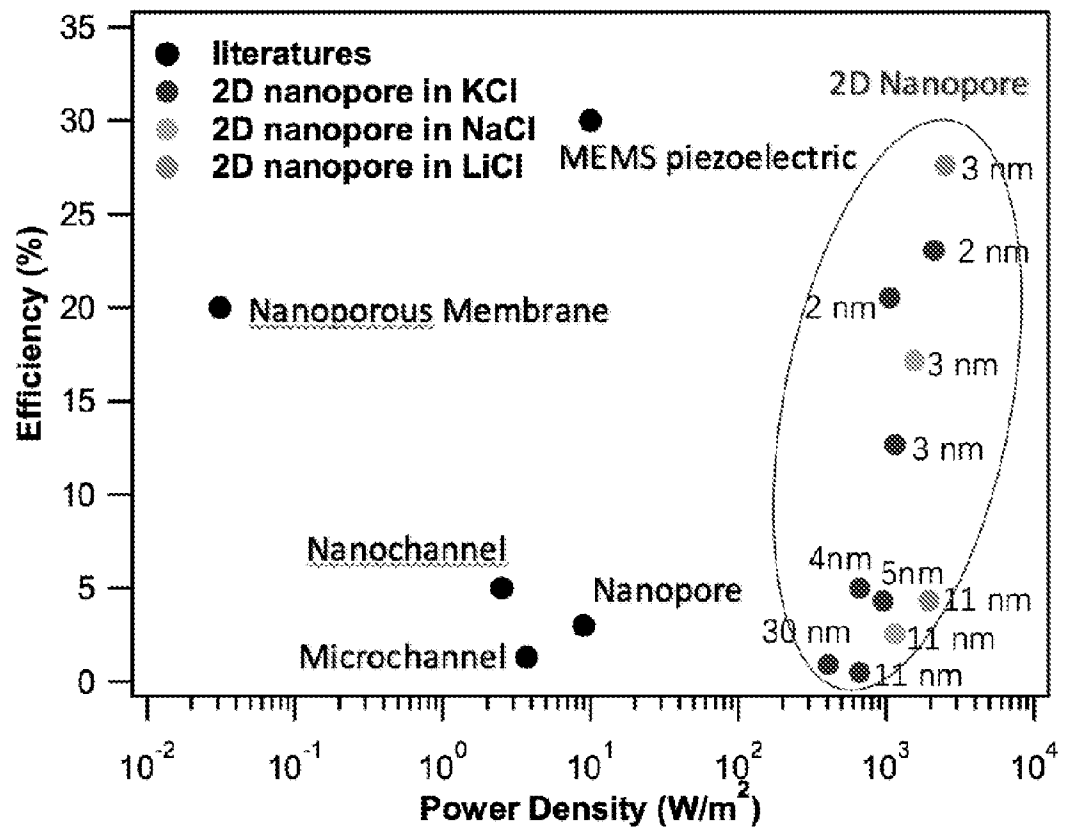
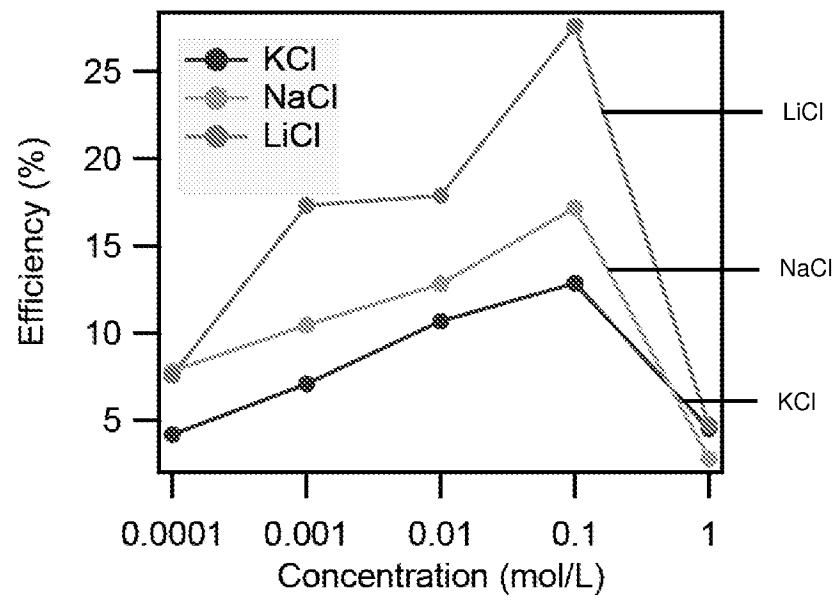


Figure 12



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2021/050035

## A. CLASSIFICATION OF SUBJECT MATTER

**H02N 3/00 (2006.01)**

According to International Patent Classification (IPC)

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H02N

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

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

FAMPAT, IEEE Xplore: energy generator, energy harvester, two-dimensional, monolayer, membrane, pore, porous, electrolyte, pressure gradient, streaming current, streaming potential, 能量发电, 能量转换, 二维, 单层, 膜, 孔, 通道, 电解液, 压力梯度, 流动电位 and other related terms

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                               | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | FENG, J. ET AL., Single-layer MoS <sub>2</sub> nanopores as nanopower generators. <i>Nature</i> , 13 July 2016, Vol. 536, pages 197-200<br>[Retrieved on 2021-04-20] <DOI: 10.1038/NATURE18593><br>Whole document                                                                                                | 1-5, 7-17             |
| X         | Two-Dimensional Nanopore And Nanoporous Devices For Molecular Sensing And Ion Selectivity. 31 December 2018<br>[Retrieved on 2021-04-20 from <a href="https://repository.upenn.edu/edissertations/2722">https://repository.upenn.edu/edissertations/2722</a> ]<br>Whole document especially pg. 37-38, 67-68     | 1-9, 12-17            |
| A         | WANG, L. ET AL., Fundamental transport mechanisms, fabrication and potential applications of nanoporous atomically thin membranes. <i>Nature Nanotechnology</i> , 6 June 2017, Vol. 12, pages 509-522<br>[Retrieved on 2021-04-20] <DOI: 10.1038/NNANO.2017.72><br>Whole document especially pg. 514 left column |                       |

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

\*Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

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"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

"&" document member of the same patent family

Date of the actual completion of the international search

20/04/2021

(day/month/year)

Date of mailing of the international search report

22/04/2021

(day/month/year)

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2021/050035

**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                 | Relevant to claim No. |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | <p>VAN DER HEYDEN, F. H. J. ET AL., Power Generation by Pressure-Driven Transport of Ions in Nanofluidic Channels. <i>Nano Letters</i>, 13 March 2007, Vol. 7, No. 4, pages 1022-1025</p> <p>[Retrieved on 2021-04-20] &lt;DOI: 10.1021/NL070194H&gt;</p> <p>Whole document especially fig. 1a</p> |                       |