(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 July 2016 (14.07.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/111649 A1

(51) **International Patent Classification**:
*H01L 41/08* (2006.01) *H01L 41/113* (2006.01)
*H01L 41/047* (2006.01)

(21) **International Application Number**:
PCT/SG2016/050006

(22) **International Filing Date**:
6 January 2016 (06.01.2016)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
62/124,887 6 January 2015 (06.01.2015) US

(71) **Applicants**: **MASSACHUSETTS INSTITUTE OF TECHNOLOGY** [US/US]; 77 Massachusetts Avenue, Cambridge, Massachusetts 02139 (US). **NANYANG TECHNOLOGICAL UNIVERSITY** [SG/SG]; 50 Nanyang Avenue, Singapore 639798 (SG).

(72) **Inventors**: **ASADNIAYE FARD JAHROMI, Mohsen**; c/o Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798 (SG). **KOTTAPALLI, Ajay Giri Prakash**; c/o Singapore-MIT Alliance for Research and Technology Centre (SMART Centre), 1 CREATE Way, #10-01 CREATE Tower, Singapore 138602 (SG). **MIAO, Jianmin**; c/o Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798 (SG). **TRIANTAFYLLOU, Michael**; c/o Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139 (US).

(74) **Agent**: **TANG, Ying**; Marks & Clerk Singapore LLP, Tanjong Pagar, P O Box 636, Singapore 910816 (SG).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17**:

— *of inventorship (Rule 4.17(iv))*

**Published**:

— *with international search report (Art. 21(3))*

WO 2016/111649 A1

(54) **Title**: ELECTRICAL DEVICE AND METHOD OF MANUFACTURING AN ELECTRICAL DEVICE

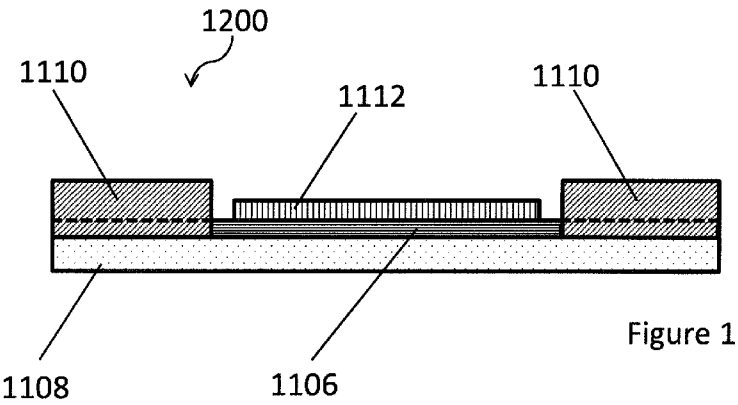



Figure 12

(57) **Abstract**: An electrical device such as a strain sensor or an energy source comprises a plurality of aligned polyvinylidene fluoride (PVDF) nano-fibers extending between a first electrode and a second electrode. Methods for manufacturing the electrical device by electrospinning the PVDF nano-fibers are also disclosed.

# ELECTRICAL DEVICE AND METHOD OF MANUFACTURING AN ELECTRICAL DEVICE

## Field of the Invention

Embodiments of the present invention relate to electrical devices such as strain sensors comprising polyvinylidene fluoride (PVDF) nano-fiber and to methods of manufacturing such devices.

## Background

During the last decade, polyvinylidene fluoride (PVDF) nano-fiber has gained remarkable interest in many applications such as energy harvesting [1], tissue engineering [2] and sensors [3]. PVDF exhibits impressive, mechanical and electrical characteristics such as piezoelectricity (highest amount the synthetic polymers), nonlinear optical properties and flexibility [4]. In the past, different methods were introduced to fabricate PVDF nano-fibers such as conventional far field electrospinning (CFFES) [5], Modified far field electrospinning (FFES) [6] and near field electrospinning (NFES) [7, 8]. The main difference between these methods is the distance between needle and collector which is higher for FFES (around 100mm) as compared to that of the NFES (1mm). Having a small emitting distance for fibers in NFES allows us to provide well aligned fibers or make them in desired forms [7]; however, PVDF fibers which are provided by this method have a larger diameter (5μm) and less flexible as compared to those provided by FFES method (1nm). The common sense in all the mentioned electrospinning methods is that the fine PVDF nano-fibers form from polymer solution under mechanical stretch and high electrostatic field. Mechanical stretch is typically induced by using the rotatory collector in FFES or by moving the Taylor cone in NFES.

Figure 1 shows a schematic view of a far field electrospinning process. As shown in Figure 1, the apparatus 100 comprises a syringe 110 which is filled with solution containing PVDF. The syringe 110 has a needle 115. A conductive planar collector 120 is arranged to collect fibers. A high voltage (HV) is applied between the needle 115 and the collector 120 by a power supply 125. When the syringe 110 is compressed, a jet of liquid is emitted which forms fiber 130. After the jet of fibers 130 flows away from the needle 115 to the collector 120, it is bent to a complex shape and forms a chaotic path which makes it difficult to electrospin aligned fibers [5] (see figure 2 which is described below). Electrical stretch is required for polling purposes.

Figure 2a shows electrospun fiber which is collected by a stationary collector. As can be seen in Figure 2a, the fibers are not aligned and follow chaotic paths. Figure 2b shows fibers collected by a rotatory collector rotating at 500 rpm. As can be seen in Figure 2b, the nano-fibers collected by the rotatory collector are aligned.

Piezoelectric crystalline structures (domains) in PVDF (β-phase) play an important role in properties of piezoelectric materials. These domains are randomly oriented in the raw material, before the poling treatment has been finished. In a more general sense, a crystal can be made piezoelectric in any chosen direction by poling treatment, which typically involves exposing the material to an electric field and elevated temperatures (for some crystals). Under the action of electric field, the material expands along the axis of the field and contracts perpendicular to that axis. The electric dipoles align and roughly stay in alignment upon solidification. In order to determine the molecular and crystalline structure of the PVDF after the electrospinning process, various characterization methods such as X-ray Diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectra can be used which are explained in [4].

PVDF is a semi-crystalline polymer with structure consisting of linear chains with sequence hydrogen and fluoride along with carbon backbone with a simple chemical formula ($CH_2$–$CF_2$). PVDF chemical structure falls between structure of Polytetrafluoroethylene (PTFE) which is ($CF_2$-$CF_2$) and Ethylene ($CH_2$-$CH_2$). While having close structure to Ethylene provides a great flexibility for PVDF, the crystalline similarity with PTFE gives stereochemical constraint to PVDF [9]. Due to this structural characteristic, PVDF forms in different crystal structures depending on sample preparation conditions. In nature PVDF appears in different phases which are known as α, β, γ and δ. Each of these phases is transferable to the others under certain external conditions. In general, α-phase is the most available phase in nature which typically obtained when the PVDF is cooled and solidified from melt. While the α-phase is known as a non-polar structure which does not show piezoelectricity, β-phase is understood as the only PVDF ferroelectric crystalline structure (polar) with strong piezoelectric effect. In general, high mechanical (approximately 50%) and electrical stretches (to align the dipoles) are required to predominantly convert the PVDF from α-phase to that of with β-phase. Table 1 provides crystallographic information of different PVDF crystalline structures [3].

| | Unit cell | Space group | Molecular chain |
|---|---|---|---|
| α-phase | A=4.96Å, b=9.64Å, c(f.a)=4.96Å | $P2_1/c$-$C_{2h}^5$ | $TG\bar{T}\bar{G}$ |
| β-phase | A=8.58Å, b=4.91Å, c(f.a)=2.56Å | $Cm2m$-$C_{2v}^{14}$ | Slightly twisted planar-zigzag |

Table 1: Crystallographic data of crystalline structures of PVDF [9]

As has been pointed out, unoriented form of PVDF (α-phase) can be achieved by casting from solution of PVDF powder dissolved into Acetone, and Dimethylacetamide (DMA). While the process of fabricating PVDF in α-phase is rather simple, more steps are required to achieve the nano-fibers with β-phase. In the past various methods have been proposed to increase the ration of the β-phase in the materials. For instance, annealing the sample at high pressure and high temperature or adding strongly polar hexamethylphosphorictriamide (HMPTA) in the solution. It is also reported that adding carbon nanotubes in the PVDF solution can increase the Young Modulus of the material and enhance the growth of the β-phase structure and provide PVDF composites fiber with improved piezoelectric properties.

Summary of the Invention

According to a first aspect of the present invention, an electrical device is disclosed. The device comprises a first electrode and a second electrode; and a plurality of aligned polyvinylidene fluoride (PVDF) nano-fibers extending between the first electrode and the second electrode.

The device may be configured as a PVDF nanofiber strain sensor. The device demonstrates high sensitivity and excellent stretchability while it does not require power supply. Thus the device may be configured as an energy source.

Embodiments of the present invention provide a highly stretchable, self-powered and ultra-sensitive strain sensor based on piezoelectric PVDF electrospun nano-fiber.

In an embodiment the aligned PVDF nano-fibers comprise beta-phase PVDF. The aligned PVDF nano-fibers may be electrospun PVDF nano-fibers.

The device may be mounted on a flexible substrate. The flexible substrate may be formed from liquid crystal polymer.

In an embodiment, the average diameter of the aligned PVDF nano-fibers is in the range 680nm to 1100nm.

According to a second aspect of the present invention, a method of manufacturing an electrical device is provided. The method comprising electrospinning polyvinylidene fluoride (PDVF) to produce nano-fibers; aligning the PVDF nano-fibers on a substrate; and forming first and second electrodes over the PDVF nano-fibers, such that the PDVF nano-fibers extend between the first electrode and the second electrode.

The electrospinning of PVDF may comprise emitting a jet of a solution comprising PVDF from a needle onto a collector. The collector may comprise the substrate on which the PVDF nano-fibers are aligned. In an embodiment, the needle is separated from the collector by a distance of between 100mm and 150mm.

In order to provide aligned the PVDF nano-fibers, in an embodiment the method further comprises rotating the collector.

In an embodiment the solution comprising PVDF has a concentration of PVDF of at least 17 wt%.

In an embodiment, the substrate is a flexible substrate. The substrate may comprise liquid crystal polymer.

The device may be a strain sensor, a self powered strain sensor or an energy source.

Brief Description of the Drawings

In the following, embodiments of the present invention will be described as non-limiting examples with reference to the accompanying drawings in which:

Figure 1 shows a schematic view of a far field electrospinning process;

Figure 2a shows nano-fibers collected on a stationary collector and Figure 2b shows nano-fibers collected on a rotating collector;

Figures 3a to 3c show the effect of PVDF concentration of electrospun nano-fibers;

Figures 4a to 4c illustrates the characterization of piezoelectric properties of PVDF nano fiber;

Figures 5a and 5b show the results of X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy on PVDF nano-fiber;

Figure 6 shows the results of Raman spectroscopy on PVDF nano-fiber;

Figures 7a-d shows nano-indentation to investigate the properties of a single PVDF nano fiber;

Figures 8a to 8e illustrate the fabrication process for a MEMS substrate for characterization of a single PVDF nano-fiber;

Figures 9a and 9b show a device for measuring the piezoelectric coefficient of a single nano-fiber;

Figures 10a and 10b show the determination of the piezoelectric coefficient of a single nano-fiber;

Figures 11a to 11f show the fabrication process of a strain sensor according to an embodiment of the present invention;

Figure 12 shows a strain sensor according to an embodiment of the present invention;

Figures 13a to 13c show an experimental demonstration of the performance of a sensor according to an embodiment of the present invention; and

Figure 14 shows a smart glove incorporating stain sensors according to an embodiment of the present invention.

Detailed Description

Electrospinning of PVDF Nano-Fiber

In this study, we used FFES process with a rotating collector to achieve aligned PVDF nano-fibers. There are various external parameters which have to be carefully optimized in order

to achieve high β-phase form PVDF with fewer beads. This part discuss on effect of electrospinning parameters on morphology and structure of the nano-fibers. Eventually, after careful optimization the parameters we electrospun the piezoelectric PVDF nano-fiber with the following process.

PVDF powder (MW 534000) was purchased from Sigma-Aldrich. A total of 1.7 g PVDF was dissolved in a mixture of 3.5mL of DMF (VWR) and 8 mL of acetone (VWR) and heated at 40 °C for 120 min so that the solution was homogeneous. The transparent viscous solution was transferred into a 1 mL syringe for electrospinning. A voltage of 12 kV was applied to the syringe needle, and a feed rate of 50 L/min was used. The electrospun fibers were collected onto a substrate, placed 15 cm away from the needle, and the fibers were electrostatically aligned across the electrode gap. This section explains optimizing of some of the important parameters of the electrospinning process to achieve effective PVDF piezoelectric nano-fibers.

a: Solution preparation

Identification of crystal form remarkably depends on solution preparation and electrospinning process parameters. In general, having a polymer solution with very high viscosity cause more beads in the electrospun fibers and if the viscosity is even higher may stuck the polymer in needle tip. Reducing the solution viscosity leads to fibers with smaller diameter and more beads. It has been reported that PVDF with concentration below 17 wt% is more likely to form beads with very less formation of fibers [10]. We used PVDF powder (MW534000) provided by Sigma eldritch. We investigated effect of polymer concentration on PVDF nano-fiber diameter for three different cases. First solution is prepared by dissolving 1.2g PVDF in 3mL of DMF (VWR) and 8 mL of acetone (VWR) PVDF. The polymer is dissolved at 70 °C for 60 min in a magnetic stirrer. For the second and third cases the PVDF ratio increased to 1.5g and 1.7g, respectively while the other effective parameters remained constant.

Figures 3a to 3c show the effect of PVDF concentration of electrospun nano-fibers. Figure 3a shows nano-fibers produced with 1.2g PVDF in polymer solution. The Fiber 302 shown in Figure 3a has a diameter of 686.82nm and the average diameter of the nano-fibers was 680nm. Figure 3b shows nano-fibers produced with 1.5g PVDF in polymer solution. The fiber 304 shown in Figure 3b has a diameter of 779.87nm and the average diameter of the nano-fibers was 780 nm. Figure 3c shows the effect of increasing the solution concentration to

1.7g PVDF. The fiber 306 shown in Figure 3c has a diameter of 1.11μm and average fiber diameter was 1.2μm.

As shown in figures 3a to 3c, by increasing the PVDF concentration in polymer solution, fibers diameter increased. The reason for forming more beads in lower polymer solution is that in this case a higher mobility of the polymer chains occurs which cause stronger instabilities of jets during the electrospinning and induce the higher stretching of the polymer and therefore, more beads appears [11]. On the other hand, higher PVDF concentration leads to a polymer solution with higher viscosity and more entanglements of the polymer chains which reduce the ability of the jet to stretch [10].

b: Electrospinning electric field

As has been mentioned, electrospinning of PVDF requires high electric field to form the fibers in β-phase form. Change in applied voltage during the electrospinning is an important external parameter which can remarkably affect the surface and quality of fibers [12]. It is reported that change in applied electric field during electrospinning process does not directly affect the morphology of the nano-fibers for certain polymers however it can alter the shape and surface.

c: nozzle-to-collector distance

The distance between Nozzle and collector is an important parameter which has influential effects on morphology and structure of the nano-fibers because of their dependence on the deposition time, evaporation rate and whipping or instability interval [13]. It is reported that decreasing the nozzle to collector distance in electrospinning of PVDF might lead to an increase in fiber diameters [10]. However, our experiment did not show a significant difference in average diameter between the electrospun fibers developed with nozzle to collector distance of 100mm and 150mm.

Piezoelectric Characteristics of a Single PVDF Nano-Fiber Sensor

This section presents a comprehensive characterization on piezoelectric properties of PVDF nano fiber. We performed electrospinning process to develop align fibers in β-phase on Aluminium foil substrate.

Figure 4a shows the electrospinning setup used to produce PVDF nano-fibers. The setup is as described above in relation to Figure 1. A solution containing PVDF was inserted into a syringe 110. The solution is emitted from the syringe 100 through a needle 115 towards the collector 120 which is formed from an Aluminium substrate. The needle 115 of the syringe 110 is connected to a high voltage (HV) power supply 125 the ground terminal of which is connected to the collector 120. Fibers 130 are formed as the solution is emitted from the syringe 110.

Figure 4b shows scanning electron microscope (SEM) images of aligned electrospun PVDF nano-fibers 410 on Aluminium foil substrate. The scale bar 420 of the main image has 30μm intervals, the inset image scale bar 430 has a length of 1μm. As shown in Figure 4b, the average diameter of nano-fibers is 800nm.

We have also succeeded in obtaining one single fibers in any desire substrate by carefully optimizing the electrospinning process (see figure 4c). Obtaining single fiber between desired electrodes is an important task which allows us to characterize the piezoelectric of single nano-fiber.

Figure 4c shows a single fiber 440 on a transmission electron microscopy (TEM) grid 450 to study the mechanical characteristic of a single PVDF nano-fiber.

X-Ray, FTIR and Raman Characterization of the Nano-Fiber

As mentioned above, developing PVDF with β-phase is a critical issue which requires careful optimization of electrospinning process and solution preparation. In order to observe the material phase after each step of optimization, we performed X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy to observe the material structure.

Figure 5a shows the XRD patterns of the PVDF nano-fibers. The XRD patterns are observed with a Siemens D5000 X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å). The tests were conducted in reflection mode at ambient temperature with two theta (degree) varying between 10° and 50°. The scanning speed was considered as $1min^{-1}$ and the step size was 0.02°. As shown in Figure 5a, there is a strong peak 510 at 20.2° for the nano-fiber which shows the β-phase is the dominate structure in the material. Interestingly, α-phase absorption bands such as 18.3° and 41.1° are not evident in the XRD pattern which indicates the existence of a very small portion of α-phase [14].

Figure 5b shows Fourier transform infrared (FTIR) spectra of the nano-fibers. Samples were placed on top of the ATR set and scanned from 600 to 1500 $cm^{-1}$. A total of 32 scans were collected for signal averaging. In this image the bands 520 seen at 840$cm^{-1}$ 1280 $cm^{-1}$ are indexed to β phase. The IR band 530 at 1180$cm^{-1}$ is unique to the form β which is well separated from the band at 1150 $cm^{-1}$ which belongs to α form. The $CH_2$ bending mode 340 of the phase β appears at 1431 $cm^{-1}$ band spectrum of the FTIR plot.

Figure 6 illustrates the Raman spectroscopy experiments on a PVDF single fiber. Structural properties of the nano-fibers are investigated using Raman spectroscopy.

As compared to FTIR and XRD, Raman spectroscopy yields bands of low wave numbers as good as bands of higher wave numbers. If a molecule possesses a centre of symmetry, the fundamentals are active in either Raman or FTIR but not in both. Thus, Raman data provide more spectroscopic information which cannot be provided by IR or XRD [15]. The structural properties of the fibers were investigated by a confocal Raman (Witec, Alpha 300) equipped with a 633 nm wavelength laser and a 50X magnification objective lens for in grating 600 for Raman shifts 500 $cm^{-1}$ - 3000 $cm^{-1}$. The machine was calibrated using a silicon wafer. The collected spectra were smoothed and filtered using Witec Project 2.04. The main peaks 610 on the plot reviled a high concentration of β-phase and therefore which leads to a high piezoelectricity for the developed nano-fibers.

Thus, the XRD and FTIR and Raman spectroscopy data demonstrate that electrospinning leads to conformation changes and enhances the b-crystalline phase.

Characterization of Mechanical Properties of a single PVDF Nano-Fiber Sensor

We have used nano-indentation study to investigate the Young modules of single PVDF nano fiber. The mechanical properties of the fibers were probed using a TriboScan 950 (Hysitron, MN, USA). The machine was equipped with a cube corner tip and the test was done in scanning probe microscope (SPM) mode.

Figures 7a-d shows the results of the study. Due to the samples size, a 50 uN load with 5s-2s-5s load function (loading-holding-unloading) was applied to the samples in piezo automation mode. Indentation points were chosen on apex of the fibers. The cube corner tip was calibrated with a standard fused quartz sample for 100 nm – 400 nm contact depths.

Figure 7a shows the elastic modulus 710 (left-hand scale) and hardness 720 (right hand scale). The nano-indentation studies of the fibers revealed that the elastic modulus and hardness of the samples were 2.2 GPa and 0.1 GPa, respectively.

Figure 7b is a load-displacement curve showing contact depth against applied load.

Figures 7c and 7d show SPM images of the position of indents (labeled as 0 to 7) on the fibers.

Determination of Piezoelectric Coefficient of a Single PVDF Nano-Fiber

In this part, piezoelectric characterization of a single PVDF nano-fiber is presented. For this purpose, we first fabricated a Micro-electromechanical system (MEMS) substrate that allows a single nano-fiber to be placed running between the electrodes.

Figures 8a to 8e illustrate the fabrication process for a MEMS substrate for characterization of a single PVDF nano-fiber.

As shown in Figure 8a, fabrication is performed on a 500μm silicon wafer 802. As shown in Figure 8b, a thick layer (1μm) $SiO_2$ was grown on top of the silicon using a plasma-enhanced chemical vapor deposition (PECVD) process as the insulator layer 804. As shown in Figure 8c, a thickness of 500nm Gold was sputtered to form the electrodes 806. As shown in Figure 8d, hydrofluoric acid (HF) etching was used to remove the $SiO_2$ layer in an area 808 between the electrodes 806. This was followed by deep reactive-ion etching (DRIE) to make a cavity 810 with depth of 300μm in the silicon wafer 802.

Figures 9a and 9b show a MEMS substrate for characterization of a single PVDF nano-fiber. Figure 9a shows the size of the MEMS substrate for characterization of a single PVDF nano-fiber 900 in relation to a Singapore 10 cent coin 902. Figure 9b shows a photograph of a MEMS substrate for characterization of a single PVDF nano-fiber 900. The substrate 900 comprises two gold electrodes 806 with a cavity 810 located between the electrodes 806. The sides of the cavity 810 are defined by a remaining part of the insulator layer 804.

Figure 10a shows a schematic diagram of the device 900 for measuring the piezoelectric coefficient of a single nano-fiber. As shown in Figure 10a, a single PVDF nano-fiber 1002 is stretched between the device's electrodes 806. The electrospinning process parameters are the optimized values which are explained above. The two ends of the suspended fiber are

fixed using conductive epoxy 1004. By applying various electrical fields to the electrodes 806 ranging from 0 to 1V/mm, the maximum deformations of fibers (at centre point) under a confocal microscope (Nikon A1R MP+ Multiphoton) at each point are observed.

The insert of Figure 10a shows a photograph of a suspended PVDF nano-fiber 1002 with diameter of 800nm and length of 400μm.

Figure 10b shows the experimental results as a graph of displacement of the centre point of the fiber against applied electric field. The experimental results showed a high piezoelectric coefficient $d_{33}$=-58.7(pm/V) for single PVDF nano-fiber.

Ultrasensitive and Stretchable Strain Sensor

There have been increasing demands for stretchable and high-sensitivity sensors for use in structure health monitoring, human motion capture, sport performance monitoring and rehabilitation [16, 17]. Such high performance myoelectric sensors are also remarkably important in developing new generation of artificial limbs where a combination of robotic actuators and sensory systems are required to provide lifelike, affordable, functional and easy to use devices that can interact with human body.

Here, we present a highly stretchable, self-powered and ultra-sensitive strain sensor based on piezoelectric PVDF electrospun nano-fiber. Complete studies on mechanical and piezoelectric characteristics of the single PVDF nano-fiber are presented. We investigate the applicability of our strain sensor on human's motion recognition by fabricating a glove embedded with two nano-fiber sensors on its middle and index fingers. We also present the performance of the proposed device in response to an oscillatory load at very low frequency (0.5Hz).

Fabrication of an Aligned Nano-Fiber Sensor

After mechanical and piezoelectric characterization of single nano-fiber, we developed an ultra-sensitive and stretchable sensor by using PVDF nano-fiber sensor. The fabrication process of the sensor is depicted in figure 11.

Figures 11a to 11f show the fabrication process of a strain sensor according to an embodiment of the present invention.

Figure 11a shows the collector which was formed from aluminium foil 1102 on a glass slide 1104. As shown in Figure 11b, aligned PVDF fibers 1106 are collected on the aluminium foil substrate 1102. The aligned PVDF fibers 1106 were electrospun using the method described above.

As shown in Figure 11c, the aligned PVDF fibers 1106 are transferred from the aluminium foil substrate 1102 to a flexible liquid crystal polymer (LCP) substrate 1108. The flexible LCP substrate 1108 has 25μm thickness; 10mm width; and 20mm length.

As shown in Figure 11d, aligned PVDF fibers 1106 are attached to the flexible LCP substrate 1108. As shown in Figure 11e, gold electrodes 1110 with dimensions 2mm width and 10mm length are fixed on the two ends of the flexible LCP substrate 1108. The electrodes 1110 overlap with the aligned PVDF fibers 1106 and the fibers 1106 run between the two electrodes 1110.

As shown in Figure 11f, a protective layer 1112 of carbon tape is placed over the aligned PVDF fibers 1106 between the two electrodes 1110.

Figure 12 shows a stretchable strain sensor based on PVDF electrospun nano-fiber according to an embodiment of the present invention.

The strain sensor 1200 comprises a plurality of aligned PVDF fibers 1106 which are disposed on a flexible LCP substrate 1108. Two electrodes 1110 are arranged with one at each end of the strain sensor 1200. The aligned PVDF fibers 1106 run from one electrode 1110 to the other electrode 1110. The electrodes 1110 are arranged over the aligned PVDF fibers 1106 and at each end of the strain sensor 1200. A protective layer 1112 of carbon tape is arranged over the aligned PVDF fibers 1106 between the two electrodes 1110. The dimensions of the strain sensor 1200 are as described above with reference to Figure 11a to 11f.

Dynamic Pressure Detection using a Dipole Stimulus

In this part, in order to evaluate the performance of the proposed sensor under dynamic pressure a vibrating sphere (dipole) is used to generate oscillatory pressure and the sensor output is observed under various frequencies. The detail of the vibrating sphere oscillator system is described in references [18] and [19].

Figure 13a shows a schematic of an experiment used to demonstrate the performance of the sensor. As shown in Figure 13a, a vibrating sphere or dipole 1302 is placed above the sensor 1200. The voltage between the electrodes 1110 is measured. The dipole 1302 is kept at the distance of 2mm above the sensor and amplitude of vibration kept constant (250mVrms) while the frequency changed from 0.5Hz to 5 Hz. The object that generates the stimulus is a stainless sphere (vibrating sphere) of 8 mm diameter, which is attached to a minishaker (model 410, B & K, Norcross, GA) through a rod of 2 mm diameter. The minishaker is driven by a sinusoidal signal generated by a function generator amplified through a power amplifier (Type 2718, B & K). Data of peak to peak amplitudes of the sensor outputs are recorded using LABVIEW software as the temperature increases. During the experiments, sensors are directly connected to a data-acquisition card without using any external electrical filters or amplifiers. To ensure the repeatability of the results, the experiment was repeated on four different sensors. Figures 13b and 13c show the sensor output 1310 as a function of time for various frequencies. In order to ensure that the output was from the sensor and not from noise, the same experiments were repeated with a sensor without PVDF nano-fiber (marked as paper 1320 in the graphs) with the same condition. Figure 13b and 13c show experimental result when the vibrating sphere shakes at frequency of 1Hz and 2HZ and amplitude of 250 mVrms.

Myoelectronic Applications of the Nano-Fiber Sensor

There is immense need for producing myoelectric limbs that could help amputees to regain independence in their everyday lives. Myoelectric sensors are required to provide signals for control of artificial limbs. Recently, there have been numerous attempts to develop strain sensors employing materials such as carbon nanomaterial or silver nanowires [1]. Although using these devices show superior performances, lack of stretchability and high power consumption make them inapplicable for many real-time situations. The proposed PVDF nano-fiber strain sensor in this work demonstrates a higher sensitivity and excellent stretchability while it does not require power supply. In order to investigate the performance of the proposed sensors in detecting the movement of human limb joints, a smart glove is developed by mounting the sensors on its fingers.

Figure 14 shows a smart glove incorporating stain sensors according to an embodiment of the present invention.

The smart glove 1400 is integrated with a data acquisition system that can transfer the sensor output to a computer. A first sensor 1410 is mounted on the index finger of the glove

1400 and a second sensor 1420 is mounted on the middle finger of the glove 1400. Figure 14 also shows the sensor output 1450 from the first sensor 1410 and the sensor output 1460 from the second sensor 1420 in response to bending the index and middle fingers.

For example, in the first case, the middle finger is bended while the index finger stayed straight. A clear peak in the sensor output 1460 from the sensor on the middle finger (plotted by red) yields the displacement of this finger while the sensor output 1450 on the middle finger (plotted in black) is almost remained unchanged. A very small change in the output of the sensor on index finger is due to the small motion of this finger while the substantial bending was occurring on middle finger. The more the fingers were bent, the more mechanical stress is induced on the nano-fibers which led to a higher sensor output. Similar explanation can be applied for the other cases when the middle remained straight, both fingers stayed unchanged and both fingers bend together. The sensor exhibited an excellent stability, response speed, and repeatability.

The nano-fiber sensors described herein have a wide range of applications ranging from robotics to the biomedical industry. In the area of wearable electronics, especially myoelectronics and artificial limbs there is an immense need for nano-fiber sensors. Being stretchable, self-powered and surface mountable there sensors may play an important role in wearable electronic devices. Since the mechanical strain applied on the sensors generates charges, the sensors could also be used as energy harvesters. These nano-sensors can function as self-powered energy sources which harvest energy from vibrations that exist in the ambient environment. These nano-fiber sensors also find important applications in sport performance monitoring. For example, large area strain sensors could be embedded in the soles of the shoes worn by a player. The strain patterns generated on the entire surface of the foot could then be visualized in situ as the person performs sporting acts.

Other possible applications include structural health monitoring, rehabilitation, biomechanics and physiology.

It is envisaged that the sensors may be packaged in packaging that perserves the key features such as stretchability and ultrahigh sensitivity.

References

[1] C. Chang, V. H. Tran, J. Wang, Y.-K. Fuh, and L. Lin, "Direct-Write Piezoelectric Polymeric Nanogenerator with High Energy Conversion Efficiency," Nano Letters, vol. 10, pp. 726-731, Feb 2010.

[2] Y.-F. Goh, I. Shakir, and R. Hussain, "Electrospun fibers for tissue engineering, drug delivery, and wound dressing," Journal of Materials Science, vol. 48, pp. 3027-3054, Apr 2013.

[3] D. Mandal, S. Yoon, and K. J. Kim, "Origin of Piezoelectricity in an Electrospun Poly(vinylidene fluoride-trifluoroethylene) Nanofiber Web-Based Nanogenerator and Nano-Pressure Sensor," Macromolecular Rapid Communications, vol. 32, pp. 831-837, Jun 1 2011.

[4] J. Chang, M. Domnner, C. Chang, and L. Lin, "Piezoelectric nanofibers for energy scavenging applications," Nano Energy, vol. 1, pp. 356-371, May 2012.

[5] D. H. Reneker, A. L. Yarin, H. Fong, and S. Koombhongse, "Bending instability of electrically charged liquid jets of polymer solutions in electrospinning," Journal of Applied Physics, vol. 87, pp. 4531-4547, May 1 2000.

[6] E. Hollenstein, M. Davis, D. Damjanovic, and N. Setter, "Piezoelectric properties of Li- and Ta-modified (K0.5Na0.5)NbO3 ceramics," Applied Physics Letters, vol. 87, Oct 31 2005.

[7] Z. H. Liu, C. T. Pan, L. W. Lin, and H. W. Lai, "Piezoelectric properties of PVDF/MWCNT nanofiber using near-field electrospinning," Sensors and Actuators a-Physical, vol. 193, pp. 13-24, Apr 15 2013.

[8] D. H. Sun, C. Chang, S. Li, and L. W. Lin, "Near-field electrospinning," Nano Letters, vol. 6, pp. 839-842, Apr 2006.

[9] H. S. Nalwa, "Ferroelectric Polymers: Chemistry: Physics, and Applications," CRC Press, vol. 20 Jun 1995.

[10] S. P. Windsor and M. J. McHenry, "The influence of viscous hydrodynamics on the fish lateral-line system," Integrative and Comparative Biology, vol. 49, pp. 691-701, Dec 2009.

[11] V. Jacobs, A. Patanaik, R. D. Anandjiwala, and M. Maaza, "Optimization of Electrospinning Parameters for Chitosan Nanofibres," Current Nanoscience, vol. 7, pp. 396-401, Jun 2011.

[12] H. Fong, I. Chun, and D. H. Reneker, "Beaded nanofibers formed during electrospinning," Polymer, vol. 40, pp. 4585-4592, Jul 1999.

[13] T. J. Sill and H. A. von Recum, "Electro spinning: Applications in drug delivery and tissue engineering," Biomaterials, vol. 29, pp. 1989-2006, May 2008.

[14] A. Baji, Y.-W. Mai, Q. Li, and Y. Liu, "Electrospinning induced ferroelectricity in poly(vinylidene fluoride) fibers," Nanoscale, vol. 3, pp. 3068-3071, 2011 2011.

[15] P. Nallasamy and S. Mohan, "Vibrational spectroscopic characterization of form II poly(vinylidene fluoride)," Indian Journal of Pure & Applied Physics, vol. 43, pp. 821-827, Nov 2005.

[16] J. Pu, X. Yan, Y. Jiang, C. Chang, and L. Lin, "Piezoelectric actuation of direct-write electrospun fibers," Sensors and Actuators a-Physical, vol. 164, pp. 131-136, Nov-Dec 2010.

[17] M. Hempel, D. Nezich, J. Kong, and M. Hofmann, "A Novel Class of Strain Gauges Based on Layered Percolative Films of 2D Materials," Nano Letters, vol. 12, pp. 5714-5718, Nov 2012.

[18] S. Pandya, Y. Yang, D. L. Jones, J. Engel, and C. Liu, "Multisensor processing algorithms for underwater dipole localization and tracking using MEMS artificial lateral-line sensors," Eurasip Journal on Applied Signal Processing, 2006.

[19] S. Coombs, "Near-field detection of dipole sources by the gold fish (carassius-auratus) and the mottled sculpin (cottus-bairadi)," Journal of Experimental Biology, vol. 190, pp. 109-129, May 1994.

Claims

1. An electrical device comprising
a first electrode and a second electrode; and
a plurality of aligned polyvinylidene fluoride (PVDF) nano-fibers extending between the first electrode and the second electrode.

2. An electrical device according to claim 1, wherein the aligned PVDF nano-fibers comprise beta-phase PVDF.

3. An electrical device according to claim 1 or claim 2, wherein the aligned PVDF nano-fibers are electrospun PVDF nano-fibers.

4. An electrical device according to any preceding claim, further comprising a flexible substrate.

5. An electrical device according to claim 4 wherein the flexible substrate comprises liquid crystal polymer.

6. A electrical device according to any preceding claim wherein the average diameter of the aligned PVDF nano-fibers is in the range 680nm to 1100nm.

7. An electrical device according to any preceding claim configured as a strain sensor.

8. An electrical device according to any one of claims 1 to 6, configured as an energy source.

9. A method of manufacturing an electrical device, the method comprising
electrospinning polyvinylidene fluoride (PDVF) to produce nano-fibers;
aligning the PVDF nano-fibers on a substrate; and
forming first and second electrodes over the PDVF nano-fibers, such that the PDVF nano-fibers extend between the first electrode and the second electrode.

10. A method according to claim 9, wherein electrospinning PVDF comprises emitting a jet of a solution comprising PVDF from a needle onto a collector.

11. A method according to claim 10 wherein the needle is separated from the collector by a distance of between 100mm and 150mm.

12. A method according to claim 10 or claim 11 further comprising rotating the collector.

13. A method according to any one of claims 10 to 12, wherein the solution comprising PVDF has a concentration of PVDF of at least 17 wt%.

14. A method according to any one of claims 9 to 13 wherein the substrate is a flexible substrate.

15. A method according to claim 14 wherein the flexible substrate comprises liquid crystal polymer.

16. A method according to any one of claims 9 to 15, wherein the electrical device is a strain sensor.

17. A method according to any one of claims 9 to 15, wherein the electrical device is an energy source.

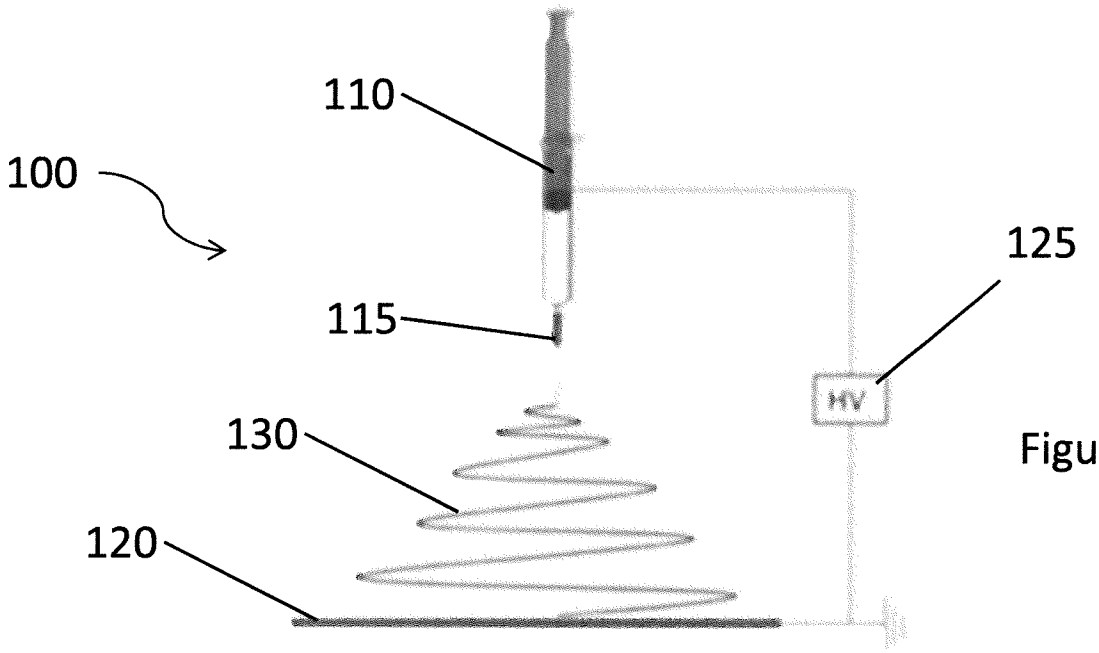



Figure 1

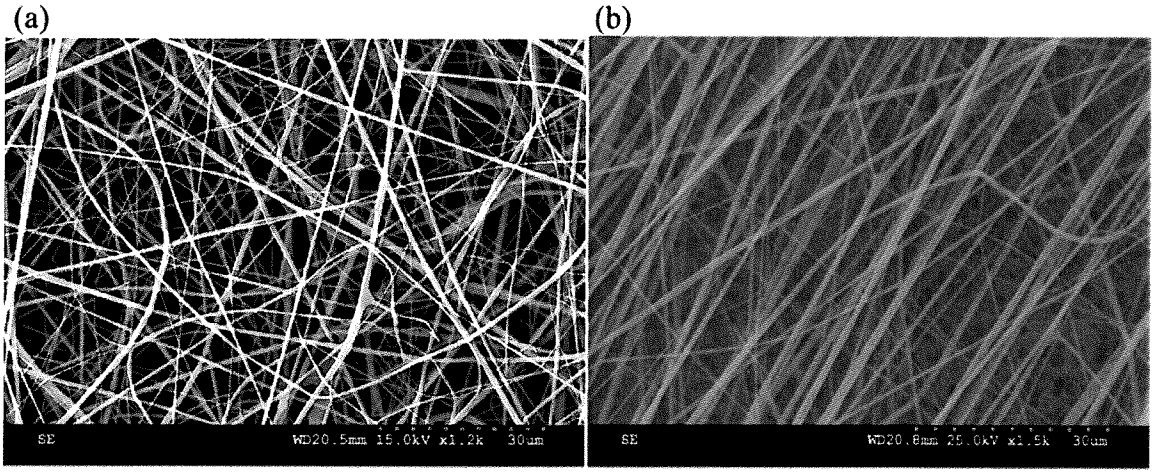



Figure 2

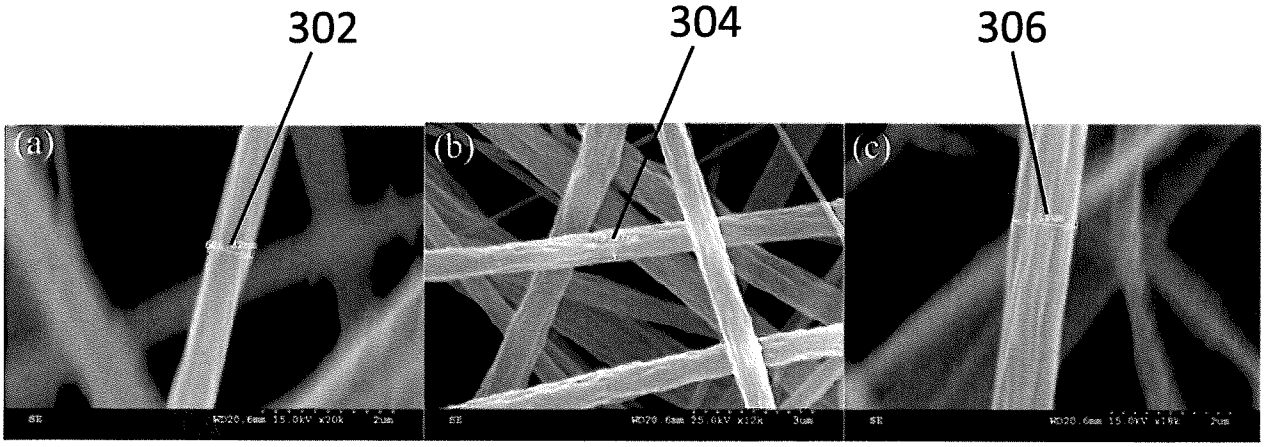



Figure 3

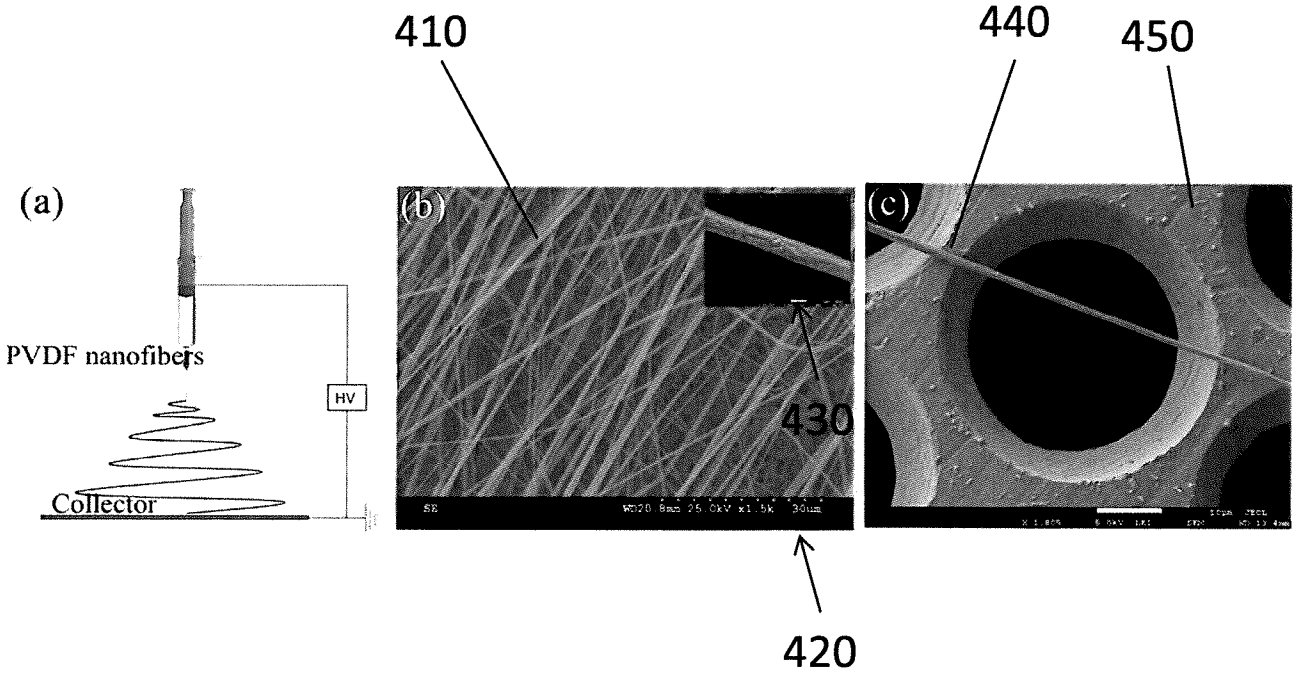



Figure 4

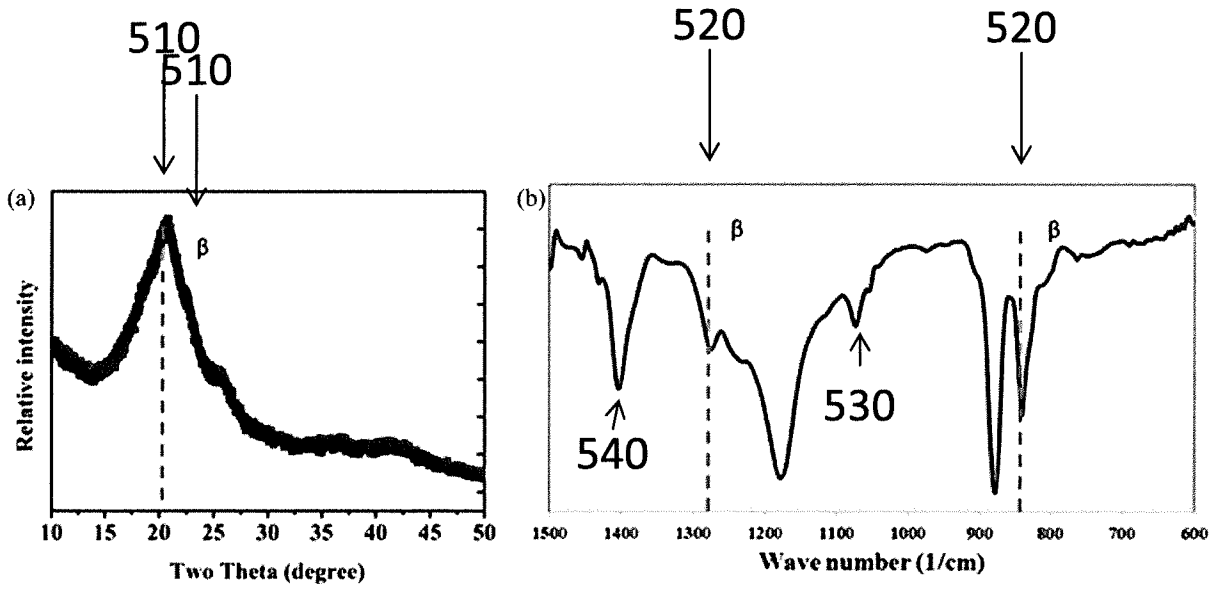



Figure 5

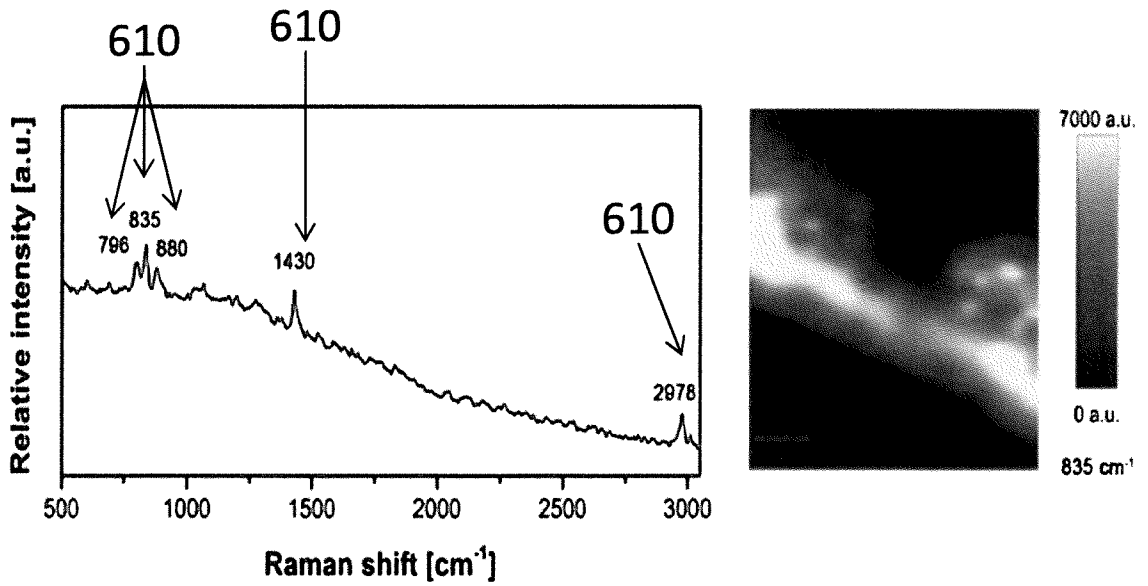



Figure 6

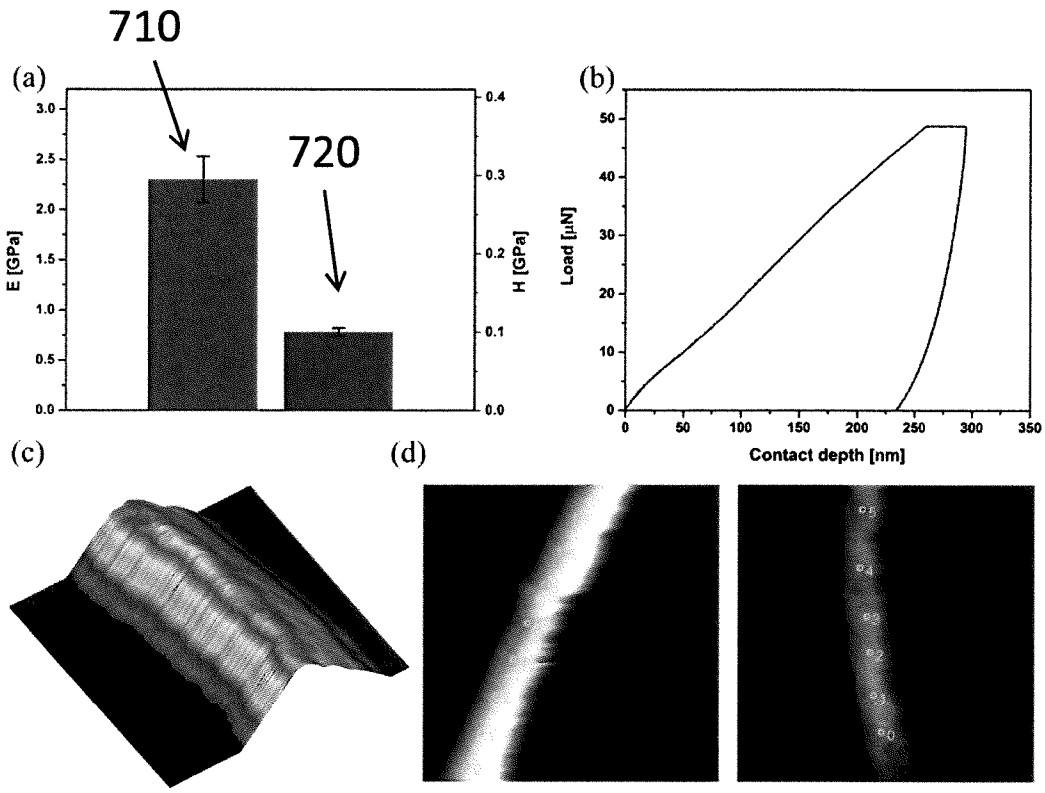



Figure 7

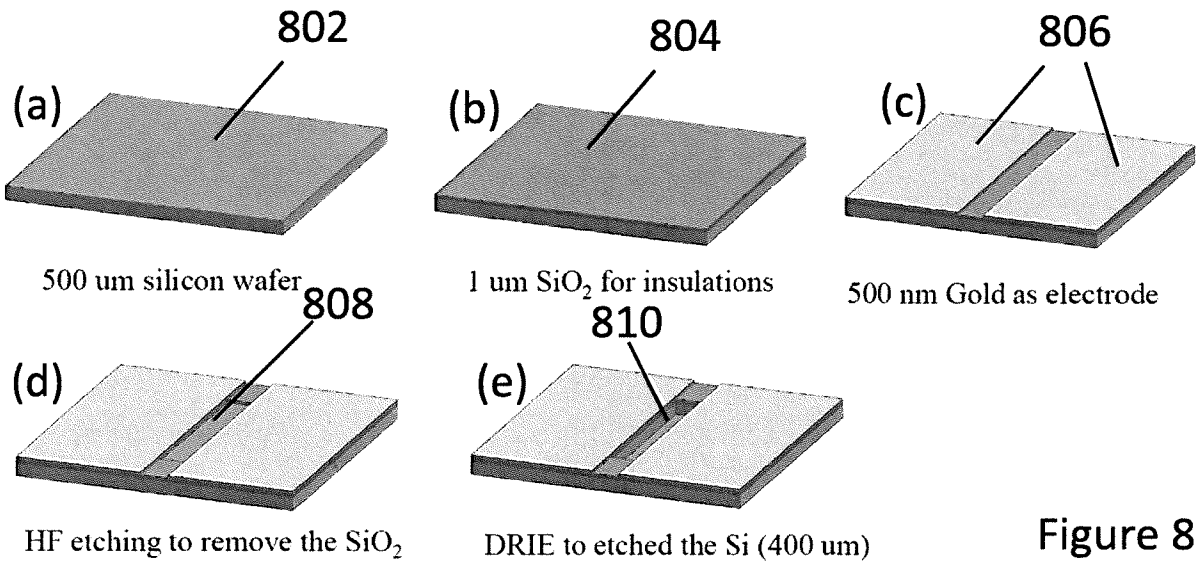



Figure 8

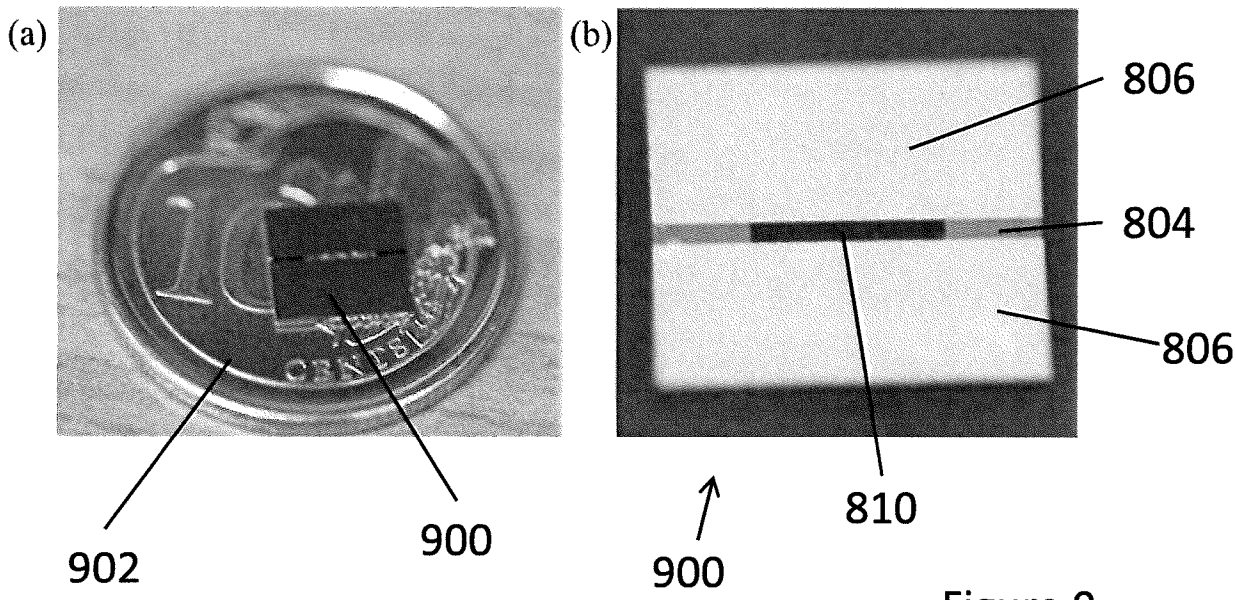



Figure 9

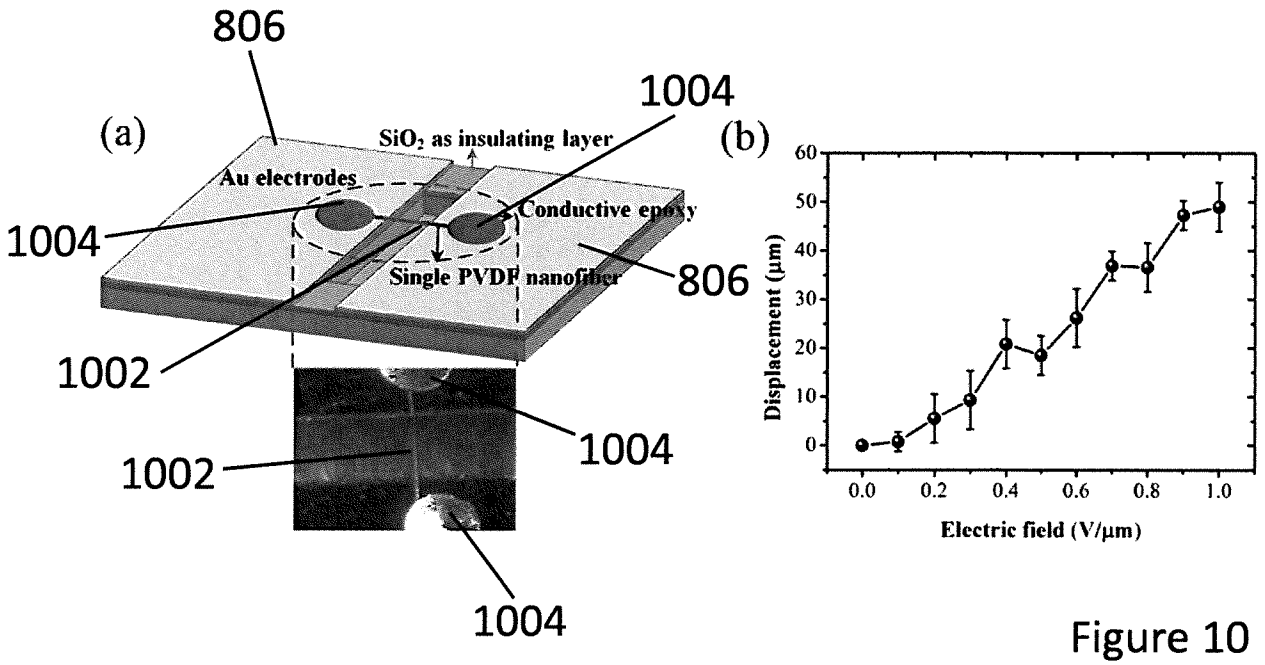



Figure 10

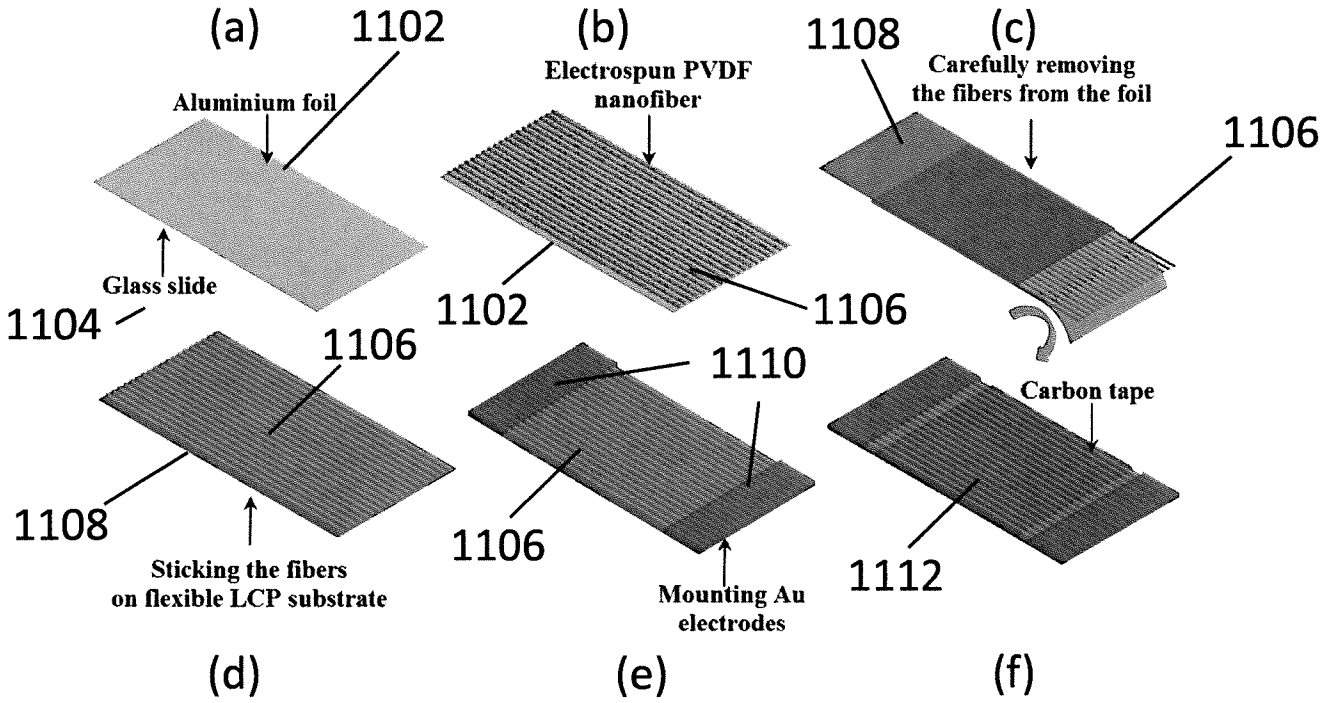



Figure 11

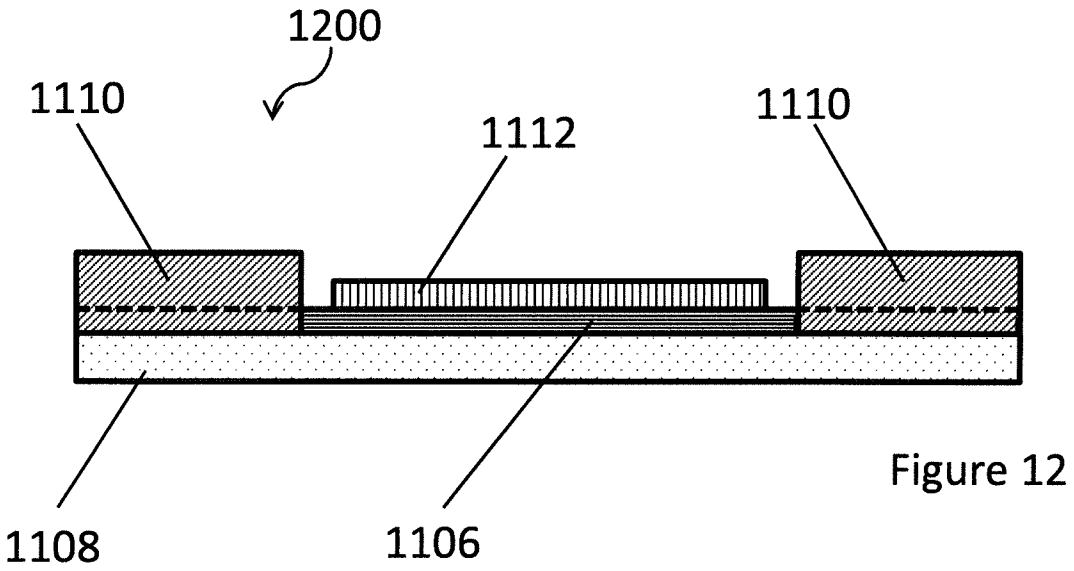



Figure 12

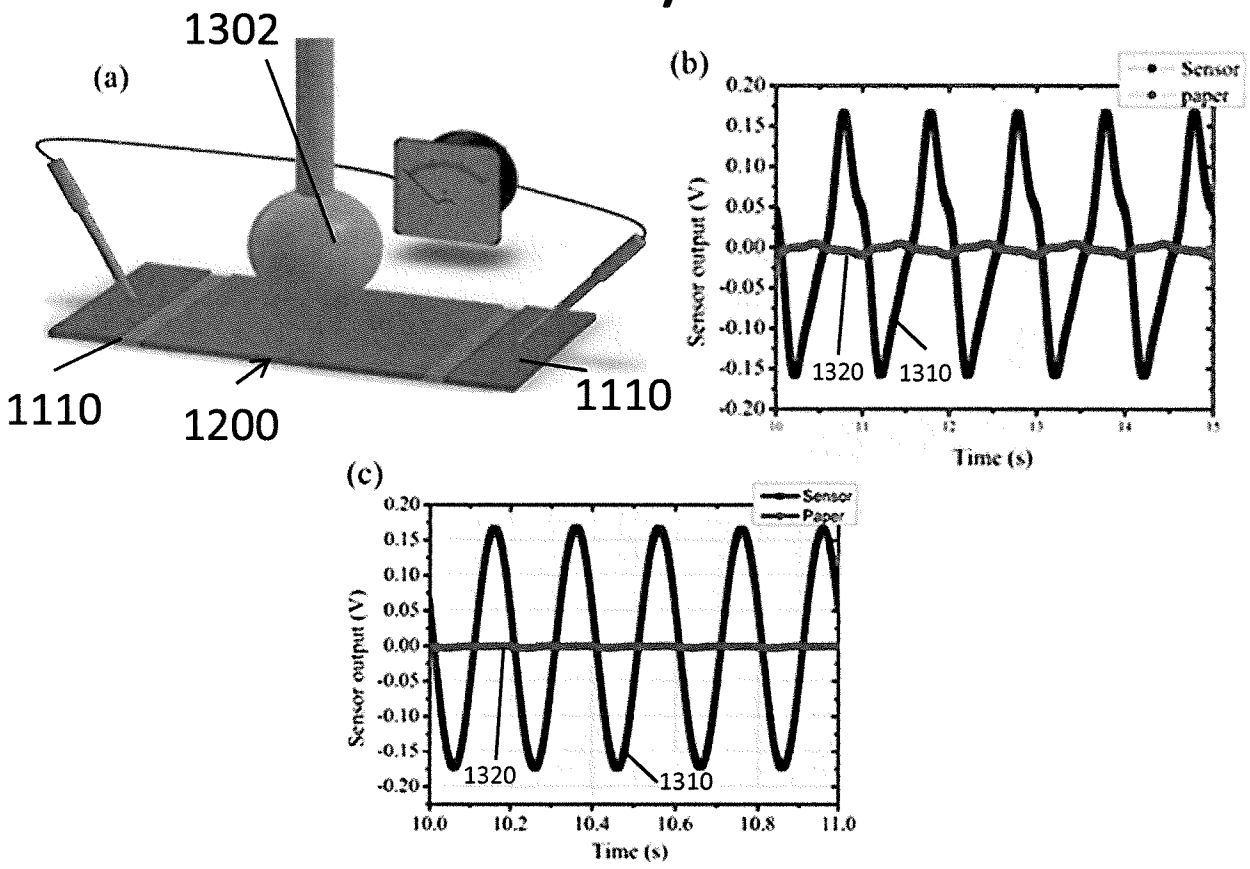



Figure 13

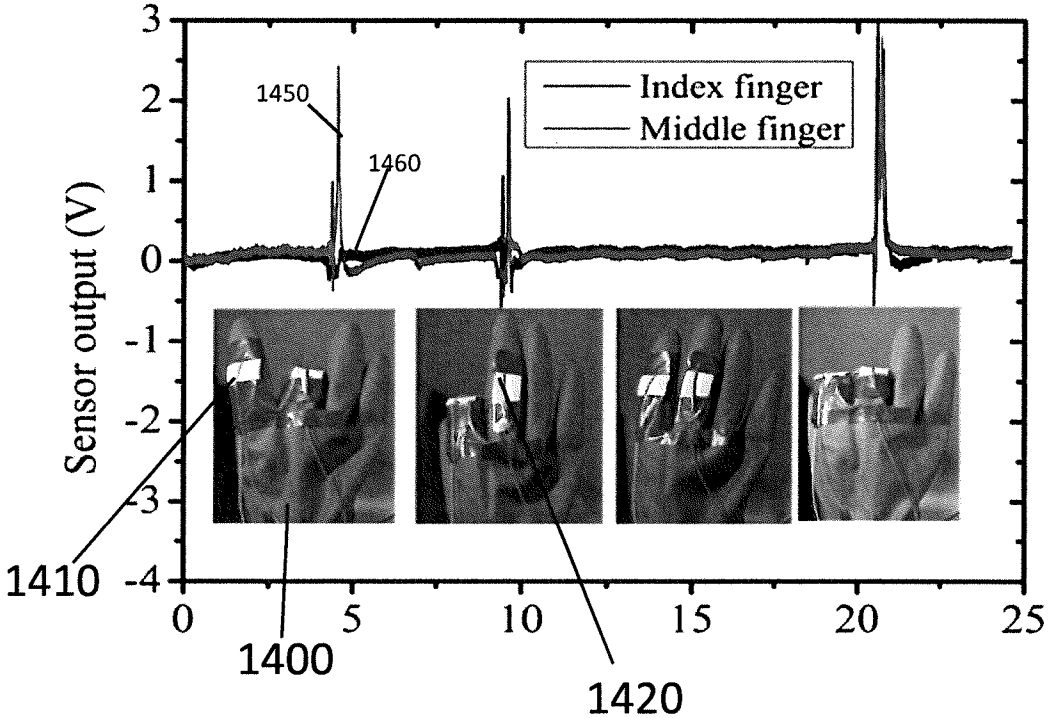



Figure 14

# INTERNATIONAL SEARCH REPORT

International application No.
**PCT/SG2016/050006**

## A. CLASSIFICATION OF SUBJECT MATTER

***H01L 41/08 (2006.01)*** ***H01L 41/047 (2006.01)*** ***H01L 41/113 (2006.01)***

According to International Patent Classification (IPC)

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01L

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/ SCOPUS: polyvinylidene, PVDF, aligned, ordered, arranged, parallel, electrospinning, electrode and like terms

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | PERSANO L. ET AL., High performance piezoelectric devices based on aligned arrays of nanofibers of poly(vinylidenefluoride-co-trifluoroethylene). *Nature Communications*, 27 March 2013, Vol. 4, No. 1633<br>[Retrieved on 2016-02-11] (DOI: 10.1038/NCOMMS2639)<br>Pg. 2-3; pg. 8 methods, discussion; figs. 1a, 1e, 3a, 3b, 4a | 1-17 |
| X | ZAMPETTI E. ET AL., Flexible piezoelectric transducer based on electrospun PVDF nanofibers for sensing applications. *Procedia Engineering*, 31 December 2014, Vol. 87, pages 1509-1512<br>[Retrieved on 2016-02-11] (DOI: 10.1016/J.PROENG.2014.11.585)<br>Abstract; pg. 1509-1510; fig. 1 | 1-17 |
| X | WO 2013/082571 A1 (GEORGIA TECH RESEARCH CORPORATION) 6 June 2013<br>Paras. [0010-0011], [0022], [0027-0028], [0033]; fig. 1c | 1-17 |

☒ 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

"E" earlier application or patent but published on or after the international filing date

"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)

"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

"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 | Date of mailing of the international search report |
|---|---|
| 11/02/2016 *(day/month/year)* | 22/02/2016 *(day/month/year)* |


Name and mailing address of the ISA/SG

IPOS INTELLECTUAL PROPERTY OFFICE OF SINGAPORE

**Intellectual Property Office of Singapore**
51 Bras Basah Road
#01-01 Manulife Centre
Singapore 189554

Email: pct@ipos.gov.sg

Authorized officer

Angelina Lim (Dr)

IPOS Customer Service Tel. No.: (+65) 6339 8616

# INTERNATIONAL SEARCH REPORT

International application No.
**PCT/SG2016/050006**

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

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | CN 103367629 A (NATIONAL CENTER FOR NANOSCIENCE AND TECHNOLOGY(NCNST) OF CHINA) 23 October 2013<br>Abstract; pg. 4; pg. 5, para. 4; pg. 7, para. 5; pg. 8, paras. 2, 6; pg. 12, para. 1; fig. 2 in the machine translation | 1-17 |
| X | EP 2945200 A1 (BEIJING INSTITUTE OF NANOENERGY AND NANOSYSTEMS) 18 November 2015<br>Paras. [0001], [0012], [0026], [0044-0045], [0059]; figs. 3-4 | 1-17 |
| A | US 2009/0056094 A1 (SHI Y. AND XU S. ) 5 March 2009<br>Whole document | - |
| A | US 2013/0038299 A1 (SOHN J. ET AL. ) 14 February 2013<br>Whole document | - |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
**PCT/SG2016/050006**

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| WO 2013/082571 A1 | 06/06/2013 | EP 2786430 A1 | 08/10/2014 |
| | | US 2012137783 A1; US 8680751 B2 | 07/06/2012 |
| CN 103367629 A | 23/10/2013 | NONE | NONE |
| EP 2945200 A1 | 18/11/2015 | CN 103779272 A | 07/05/2014 |
| | | KR 20150110590 A | 02/10/2015 |
| | | US 2015357374 A1 | 10/12/2015 |
| | | WO 2014108012 A1 | 17/07/2014 |
| US 2009/0056094 A1 | 05/03/2009 | US 8093786 B2; US 2011210650 A1 | 01/09/2011 |
| | | US 2011209820 A1 | 01/09/2011 |
| US 2013/0038299 A1 | 14/02/2013 | EP 2565952 A3; EP 2565952 A2 | 06/03/2013 |
| | | KR 20130017343 A | 20/02/2013 |