

(43) International Publication Date
12 February 2015 (12.02.2015)

(51) International Patent Classification:

H01L 41/113 (2006.01) *H01L 41/31* (2013.01)
H01L 41/053 (2006.01) *H01L 51/00* (2006.01)
H01L 41/18 (2006.01) *H02N 2/18* (2006.01)

(21) International Application Number:

PCT/AU2014/000789

(22) International Filing Date:

8 August 2014 (08.08.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

20133903001 9 August 2013 (09.08.2013) AU

(71) Applicant: MONASH UNIVERSITY [AU/AU]; Wellington Road, Clayton, VIC 3800 (AU).

(72) Inventors: WINTHER-JENSEN, Bjorn; 1/7 Kevin Street, Mount Waverley, VIC 3149 (AU). NAIR, Santhosh, Sankaranarayanan; 1/1 Beddoe Avenue, Clayton, VIC 3168 (AU). KOLODZIEJCZYK, Bartłomiej; 63 Mills Street, Middle Park, VIC 3206 (AU).

(74) Agent: SMOORENBURG PATENT & TRADE MARK ATTORNEYS; PO Box 515, Ringwood, VIC 3134 (AU).

(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, LT, 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, 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).

Published:

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

(54) Title: NANOGENERATORS AND A METHOD FOR THEIR MANUFACTURE

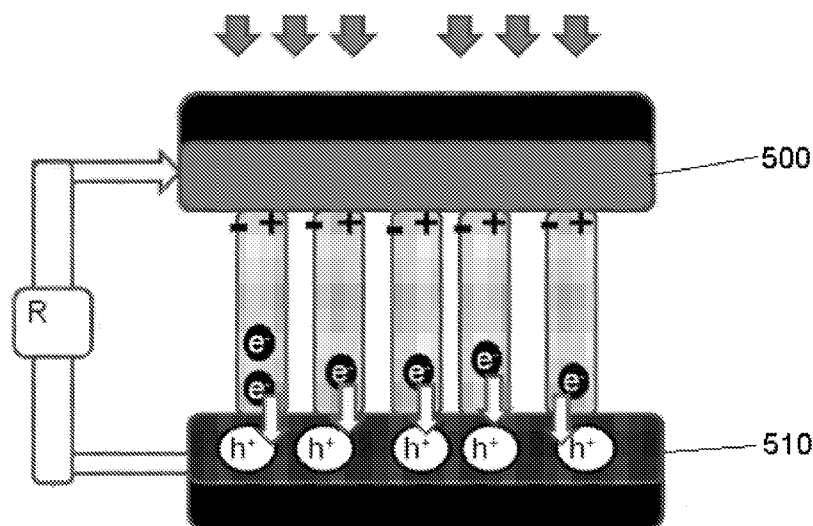


FIGURE 5(b)

(57) Abstract: The invention relates to a nanogenerator comprising a p-type conducting polymer substrate and a piezoelectric material, the p-type conducting polymer substrate preferably being a polythiophene. The nanogenerator of the invention is preferably suitable for incorporation in porous or non-porous material, such as the warp or weft of a woven textile.

NANOGENERATORS AND A METHOD FOR THEIR MANUFACTURE

FIELD OF INVENTION

[0001] The present invention relates to the field of nanogenerators, more particularly piezoelectric nanogenerators (NGs).

[0002] In one form, the invention relates to a new fabrication technique for NGs.

[0003] In another form the invention relates to new NG power sources for devices having low power demand.

[0004] In one particular aspect the present invention is suitable for use as a power source for small personal electronic devices.

[0005] It will be convenient to hereinafter describe the invention in relation to the polymer known as PEDOT, however it should be appreciated that the present invention is not limited to that polymer component only and that other p-type polymers are suitable. Furthermore, it will also be convenient to hereinafter describe the invention with reference to the use of ZnO, which is a well known piezoelectric and pyroelectric inorganic semiconducting material used for electromechanical and thermoelectrical energy conversion. However it should be appreciated that the present invention is not limited to ZnO and that other piezoelectric materials are suitable.

BACKGROUND ART

[0006] It is to be appreciated that any discussion of documents, devices, acts or knowledge in this specification is included to explain the context of the present invention. Further, the discussion throughout this specification comes about due to the realisation of the inventor and/or the identification of certain related art problems by the inventor. Moreover, any discussion of material such as documents, devices, acts or knowledge in this specification is included to explain the context of the invention in terms of the inventor's knowledge and experience and, accordingly, any such discussion should not be taken as an admission that any of the material forms part of the prior art base or the

common general knowledge in the relevant art in Australia, or elsewhere, on or before the priority date of the disclosure and claims herein.

[0007] **Nanogenerators Generally:** Nanogenerators convert mechanical/thermal energy as produced by small-scale physical change into electricity and are typically piezoelectric (NG), triboelectric (tNG), or pyroelectric (pNG). Both the NGs and tNGs can convert mechanical energy into electricity. pNGs harvest thermal energy from a time-dependent temperature fluctuation.

[0008] Although NG, pNG and tNG research is still in its early phases, they are regarded as a breakthrough in miniaturisation of energy harvest and supply to small electronic devices. Ultimately, further development may lead to much larger energy harvesting applications.

[0009] In practice, an NG comprises a small electronic chip that can use mechanical movements of the body such as a finger pinch or footstep to generate energy. The energy is sufficient to power conventional electronics such as light emitting diodes (LEDs), liquid crystal displays (LCDs) and laser diodes in small electronic devices such as implanted medical devices, smart phones and other personal devices. In the future, further development may lead to the use of NGs for large scale applications that use periodic kinetic energy from wind or wave motion.

[0010] The electronic chip usually comprises an integrated circuit having components made from silicone and a piezoelectric ceramic, etched onto a flexible surface and small enough to be held on a finger.

[0011] The key components of an NG are nanowires (NWs) or similar structures made from piezoelectric ceramic material having a Wurtzite structure, such as ZnO, CdS or GaN. Each nanowires is typically 0.5 to 5 micron in length and about 10 to 100 nanometer diameter. Piezoelectric materials (in this case a wurtzite structured semiconducting nanostructured material), can generate a current (piezopotential) when a physical force is applied and it is bent or otherwise physically stressed.

[0012] The piezopotential can be channelled by employing the right kind of metal-semiconductor pathways/barriers such as a p-n junction by virtue of the coupling of piezoelectric and semiconducting properties. This would include for example, an ITO (Indium tin oxide) electrode.

[0013] Put simply, the NG comprises vertically oriented NWs between a base electrode and a counter electrode. The motion of the counter electrode induces the physical stress on the nanowires. The NG is integrated onto a flexible substrate.

[0014] The earliest NGs comprised ZnO NWs grown on conducting glass such as indium tin oxide (ITO) sandwiched with a gold-coated electrode.

[0015] Figure 1 illustrates the principal of how a nanogenerator works when an individual nanowire is subjected to force (F) exerted parallel to the longitudinal axis of the nanowire (Figure 1(c)) and perpendicular to the nanowire (Figure 1(d)).

[0016] Figure 1(c)(i) illustrates an AFM tip being swept through the tip of the nanowire. Only the negatively charged portion will allow the current to flow through the interface. The piezoelectric effect will create the electrical field inside the nanostructure. The stretched part with the positive strain will exhibit the positive electrical potential, whereas the compressed part with the negative strain will show the negative electrical potential. This is due to the relative displacement of cations with respect to anions in its crystalline structure. As a result, the tip of the nanowire will have an electrical potential distribution on its surface, while the bottom of the nanowire is neutralized since it is grounded.

[0017] Figure 1(c)(ii) illustrates the nanowire integrated with the counter electrode with AFM tip-like grating. The electrons are transported from the compressed portion of nanowire to the counter electrode because of Schottky contact.

[0018] Figure 1(d)(i) shows a vertically grown nanowire stacked between the ohmic contact at its bottom and the Schottky contact at its top. When the force is applied toward the tip of the nanowire, a uniaxial compression is generated in the nanowire. Due to the piezoelectric effect, the tip of the nanowire has a negative piezoelectric potential,

increasing the Fermi level at the tip. As a result the electrons will then flow from the tip to the bottom through the external circuit and a positive electrical potential will be generated at the tip. The Schottky contact will barricade the electrons being transported through the interface which will maintaining the potential at the tip. As the force is removed, the piezoelectric effect diminishes, and the electrons flow back to the top to neutralize the positive potential at the tip. Figure 1(d)(ii) illustrates generation of an alternating current output signal.

[0019] If hundreds of flexible nanowires are be packed side by side in a space less than the width of a human hair, even the slightest movement can generate current. These two-dimensional NGs can be stacked to form a three-dimensional structure, significantly increasing the current output.

[0020] **Nanogenerator Theory:** The energy harvesting ability of NGs based on the coupling of semiconducting and piezoelectric properties was first observed by the research group of Z.L Wang during the contact mode conductive AFM study of aligned ZnO nanowires (ZnO NWs) grown on α -Al₂O₃ using a Pt coated Si tip.[1]

[0021] Nanoscale mechanical energy harvesting was made possible by the Schottky barrier established between the Pt coated Si tip and ZnO NWs and the ohmic contact between silver paste and bottom of the ZnO NWs. Wang et al have demonstrated a direct current generator driven by ultrasonic waves based on this principle.[2] This kindled interest among the materials research community and generated reports of NGs based on other wurtzite structured piezoelectric semiconducting two-dimensional nanostructures comprising materials such as zinc oxide (ZnO), cadmium sulfide (CdS), zinc sulfide (ZnS), gallium nitride (GaN) and indium nitride (InN).[3]

[0022] NGs with different geometrical configurations and different components including paper and fibre substrates have since been developed.[3] Various materials such as graphene, carbon nanotube network, P3HT and PEDOT:PSS have been reported as replacement for the top gold electrode which was designed to establish a Schottky barrier with ZnO NWs.[4-7]

[0023] In the past, PEDOT:PSS has been considered as a replacement for the Schottky barrier electrode [8] but has not met with success. Specifically, attempts have been made to apply the polymer to the NG assembly by spin coating of PEDOT:PSS colloidal solution. This proved unsuccessful because PEDOT:PSS is highly acidic due to the presence of excess PSS stabilizer and the pH of commonly available solutions is as low as 1-3 at 25°C.[9] ZnO NWs dissolve at pH of about 4.5 or less.[10] Moreover if the acidic PEDOT:PSS contacts the ITO (Indium tin oxide) layer in the NG, Indium may start migrating to the organic layer which poisons the PEDOT:PSS and the inherent conductivity of the ITO is lost.[11]

[0024] In a NG assembly, ZnO NWs are generally grown on substrates which form an ohmic contact so that a transient flow of electrons are feasible between two ends of NWs when the NWs are flexed. The use of n-SiC and n-Si does not enhance the efficiency of NG, so other materials such as Ag, Ti foil, Al foil, graphene and ITO have been tested only as cost effective or more flexible options.[14,15] Commercially available ITO coated PES/PET with predefined conductivity has been widely exploited due the ease of handling. But unfortunately ITO coated PET/PES has limited flexibility and increases the resistance by 400 times due to microcracks that develop during flexing cycles.[16]

[0025] Piezoelectric inorganic semiconducting materials used for electromechanical and thermoelectrical energy conversion are relatively well known. For example in US patent 7705523 Wang describes a dye-sensitized solar cell including ZnO nanowire arrays grown on a flat substrate for harvesting solar energy is integrated with a piezoelectric nanogenerator for harvesting ultrasonic wave energy. Operation of the nanogenerator is dependent on solar energy and requires an additional power generating unit.

[0026] Several inventions have also been described that incorporate nanoscale piezoelectric devices such as US-8039834 (Zhong), EP1964161 (Song), Hyunjin Kim et al [31] and Yong Qin [35]. These prior art publications relate to different structures, but typically all include nanowires grown on a conducting glass, which is relatively inflexible.

[0027] By contrast Min-Yeol Choi et al [32] teaches the use of a ZnO nanorod array grown on a flexible, transparent indium tin oxide/PES substrate. Briscoe et al [33]

discloses ZnO nanorods grown on ITO followed by deposition of PEDOT:PSS on nanorods, with gold contacts spluttered onto the PEDOT:PSS layer. This creates a structure comprising ITO-ZnO seed – ZnO nanorods- PEDOT:PSS.

[0028] PuXian Gao et al [34] teaches a technique for growing ZnO nanowires on flexible plastic substrates, namely 50 μ m thick Dupont Kapton polyimide films.

[0029] However many of the conformations of the prior art have significant disadvantages associated with their manufacture. For example many of the nanogenerators of the prior art are relatively complicated to manufacture, requiring expensive techniques and equipment such as vacuum or clean room processing. Others are expensive to manufacture due to the high cost of components.

[0030] Another disadvantage of nanogenerators of the prior art is that they generate very low currents and voltage, due to limitations to their structure at a molecular level structure, or their lack of flexibility.

SUMMARY OF INVENTION

[0031] An object of the present invention is to provide a NG having improved power generation characteristics.

[0032] Another object of the present invention is to provide a NG having improved structure.

[0033] Another object of the present invention is to provide a convenient manufacturing method for NGs.

[0034] A further object of the present invention is to alleviate at least one disadvantage associated with the related art.

[0035] It is an object of the embodiments described herein to overcome or alleviate at least one of the above noted drawbacks of related art systems or to at least provide a useful alternative to related art systems.

[0036] In a first aspect of embodiments described herein there is provided a nanogenerator comprising a p-type conducting polymer substrate and a piezoelectric material

[0037] Preferably the p-type conducting polymer is chosen from the group comprising polythiophenes, such as, for example poly(3,4-ethylenedioxythiophene) (PEDOT), or poly-bi-thiophene and poly-ter-thiophene. Although poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT-PSS) has been used as a second electrode in NGs and PEDOT-PSS and poly (3-hexylthiophene) has been used for coating of ZnO nanowires in similar devices, p-type conducting polymers have not hitherto been used as a substrate for growing the piezoelectric nanowires which appears to be crucial to the performance of the NG.

[0038] Preferably the piezoelectric material is an n-type semi-conductor, one or more metals or a combination thereof. More preferably the piezoelectric substrate is zinc oxide, ZnO in the form of nanowires. It is particularly preferred that the piezoelectric properties of the material are coupled with semiconducting properties in such as way that a strain field is created and charge separation occurs across the nanowire when it is bent or otherwise physically stressed. This provides the basis for converting mechanical, vibrational or hydraulic energy into electricity for powering nanodevices.

[0039] Preferably the nanogenerators further comprises a second electrode of metal (e.g. gold or Ag) or PEDOT.

[0040] The present invention provides a novel method to enhance the p-n junction and improve the robustness of NG design by growing n-type ZnO directly on a p-type conducting polymer (such as PEDOT) and thus fabricate NGs of improved current generation efficiency and voltage. For example, the present invention can provide NGs having a current generation efficiency approximately 10^6 times higher than an ITO grown NG and approximately 10^2 times greater in voltage compared to the traditional design.

[0041] Without wishing to be bound by theory, it is believed that there is significantly improved contact between the p-type conducting polymer and the piezoelectric substrate and this causes the higher power generation. Again, without wishing to be bound by

theory, this improvement is believed to be linked both to the more flexible nature of the p-type conducting polymer (compared to the conducting silicone glass of the prior art) and the junction obtained between the polymer and the nanowires.

[0042] It is also noted that nanogenerators of the prior art suffer from reduced performance due to nanowires breaking away from the substrate. This is assumed less likely in the nanogenerators of the present invention due to the more flexible nature of the junction between the nanowires and the p-type polymer substrate.

[0043] A further advantage is that the thickness of the p-type polymer substrate can be optimised so that it acts as a capacitor, stabilising voltage and power flow and suppressing any voltage or power spikes.

[0044] In a second aspect of embodiments described herein there is provided a method of manufacturing a nanogenerator comprising the step of growing an n-type piezoelectric material directly on a p-type conducting polymer substrate.

[0045] Typically the method of manufacturing is carried out at low temperature, preferably less than 95°C. The principle limitation to the temperature used is the softening or degradation point of the p-type polymer substrate.

[0046] The pressure used is typically ambient, but high pressure may be convenient if the manufacture includes use of an autoclave of the like.

[0047] Typically the method includes the step of vapour phase synthesis such as vapour phase polymerisation or oxidative chemical vapour deposition. These vapour phase techniques are preferred, for example to aqueous chemical synthesis or other solvent based techniques which may lead to swelling due to the hygroscopic nature of the polymer. Vapour phase polymerization (VPP) is a flexible technique for obtaining high quality conducting polymer thin films on a variety of substrates without any compatibility issues.[8]

[0048] Preferably the method of the present invention includes application of the oxidant to the substrate using wet chemical techniques with a monomer being delivered from the vapour phase.

[0049] Nanogenerators according to the present invention may be created in any convenient conformation. They may be conformed in two-dimensions as a lateral nanowire integrated nanogenerator (LING) or in three-dimensions as a vertical nanowire integrated nanogenerator (VING). Alternatively, they may have some other conformation, such as a fabric-like geometrical configuration mentioned above.

[0050] VPP on flexible substrates can be used to achieve desirable work function, conductivity and proper energy level alignment at the ZnO-polymer interface thus eliminating the use of expensive and less efficient electrodes like ITO and Au. This approach can be extended to fibre substrates making them more suitable for wearable energy harvesting with 100 times improved efficiency compared to ITO sandwiched fibre NG.

[0051] Hence the p-type polymer can be applied on a flat surface or grown in a 'fibrous' form like a textile. For example, the p-type polymer can be applied as a flat film on a carrier polymer (eg PET) or it can be in the form of coating on (nano) fibres, such as those obtained from electro-spinning processes. In contrast to the present invention, prior art attempts to achieve a fibrous conformation have been associated with generation of extremely low currents.

[0052] In a particularly preferred embodiment the present invention comprises a pair of microfibers twined to form the nanogenerator. As the fibre is stretched the deformation of the nanostructure occurs on the stationary microfiber, resulting in voltage generation.

[0053] In another aspect of embodiments described herein there is provided an NG according to the present invention when used to power a small electronic device, or charge an electronic device.

[0054] Typically the small electronic device is a medical or veterinary device for regulating or monitoring patient health. These include implants such as pacemakers, continuous glucose monitoring systems and pharmaceutical dosage systems. Alternatively the small electronic device may be a personal device such as an iPods or smart phone. In one embodiment the present invention is used in the charging of an electronic device such as a capacitor or a battery.

[0055] In yet a further aspect of embodiments described herein there is provided a porous material or a non-porous material comprising NGs according to the present invention. In a particularly preferred embodiment the material is a textile.

[0056] In a preferred embodiment the NGs are embedded in a worn item such as clothing, shoes, belts, or clothing accessories. In a particularly preferred embodiment the NGs are incorporated into the composition or weave of the worn item, such as the warp or weft of the weave. For example, NG nanofibres according to the present invention could be woven into a knitted item.

[0057] Preferably the material, such as a textile, has at least one inner surface and at least one outer surface, the inner surface comprising nanogenerators.

[0058] Other aspects and preferred forms are disclosed in the specification and/or defined in the appended claims, forming a part of the description of the invention.

[0059] In essence, embodiments of the present invention stem from the realization that replacement of conducting glass substrates in NGs with certain conducting polymers can provide significant improvements in power generation. As compared with NGs of the prior art having similar geometries, the NG of the present invention can provide a 10^6 fold increase in currents and 10^3 fold increase in voltage.

[0060] Advantages provided by the present invention comprise the following:

- improved power generation,
- increased flexibility,

- simple design,
- low fabrication cost,
- more effective use of a renewable resource (kinetic energy from body movement), and
- more environmentally friendly utilisation of materials than batteries, reducing waste and disposal.

[0061] Further scope of applicability of embodiments of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the disclosure herein will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0062] Further disclosure, objects, advantages and aspects of preferred and other embodiments of the present application may be better understood by those skilled in the relevant art by reference to the following description of embodiments taken in conjunction with the accompanying drawings, which are given by way of illustration only, and thus are not limitative of the disclosure herein, and in which:

- Figure 1 illustrates SEM images of ZnO NWs grown on PEDOT functionalized 2-D PES (Figure 1a); and ZnO NWs grown on PEDOT functionalized 3-D PES (Figure 1b); and diagrams of relevant nanogenerators (Figure 1c and Figure 1d) showing the piezoelectric (ZnO) nanowire 101 having a Schottky contact at one end 105 and an Ohmic contact 110 at the other end.
- Figure 2 illustrates I-V curves obtained for four sandwich structures forming an NG, namely ITO+ZnO-Au (Figure 2(a)), PEDOT+ZnO-Au (Figure 2(b)), ITO+ZnO-

PEDOT (Figure 2(c)), and PEDOT+ZnO-PEDOT, wherein the structures comprise ITO (200), ZnO NWs (205), Au (210), and PEDOT (215).

- Figure 3 illustrates plots of PEDOT-ZnO-Au NG performance in terms of current (Figure 3a) and voltage (Figure 3b);
- Figure 4 shows plots illustrating a comparison of current generated by ITO NG (400) and PEDOT NG (405) in terms of current (Figure 4a) and voltage (Figure 4b);
- Figure 5 illustrates for comparison, an indium tin oxide (ITO) based NG (Figure 5a) comprising a layer of Au coated PES (500) and a layer of ITO coated PES (505) and a PEDOT based NG (Figure 5b) comprising a layer of Au coated PES (500) and PEDOT coated PES (510);
- Figure 6 illustrates plots of the performance of a PEDOT-ZnO-PEDOT NG device in terms of current (Figure 6a) and voltage (Figure 6b); and
- Figure 7 illustrates the differences between n-type and p-type films. In particular Figure 7(a) illustrates performance of a PEDOT sandwiched PEDOT fibre NG (700) and an ITO sandwiched PEDOT fibre NG (705), the drawing indicating the combination of PEDOT coated PES (715), ZnO (720) and PEDOT coated electrospun PES (725) used. Figure 7(b) illustrates the performance of a PEDOT sandwiched PEDOT fibre NG (730) and an ITO sandwiched PEDOT fibre NG (735) the drawing indicating the combination of PEDOT coated PES (715), ZnO (720) and PEDOT coated electrospun PES (725) used.

DETAILED DESCRIPTION

[0063] Preferably the method of the present invention includes vapour phase polymerization (VPP) wherein oxidant is applied to the substrate using wet chemical method and monomer is delivered from the vapour phase. A modified base inhibited VPP of PEDOT has demonstrated conductivity as high as 1000 S/cm. By comparison PEDOT:PSS spin coated layers of the prior art generally exhibit 10 S/cm.[19]

[0064] VPP polymerized PEDOT has shown good conductivity, chemical and mechanical stability and comparable work functions, and thus may be used to replace ITO/Au in NGs. The following example demonstrates the VPP of a conducting polymer - PEDOT on PES (flexible 2-D PES and fibre substrates 3-D PES) and growth of ZnO NWs using low temperature aqueous growth technique on the PEDOT coated substrates. These hybrid structures have been tested to assess their potential for piezoelectric energy harvesting.

[0065] The following non-limiting example demonstrates a relatively simple method for fabricating of a more efficient NG by growing n-type ZnO on a p-type polymer to produce a stable ZnO-polymer interface. Without wishing to be bound by theory, it appears that the reversibility of Schottky barrier into ohmic is not universal, and instead the top electrode will always have a tendency to gate the piezo-generated electrons.

[0066] The use of a p-type polymer functionalised electrode as the ohmic contact increases the performance of NG due to the combined effect of screening of carrier density and functioning of 3 different p-n junctions simultaneously. Polymer-ZnO p-n junctions reduce the screening electron available in the system and in addition, mechanical flexibility increase the statistical number of energy generating events in the device. Thus, polymer-NG can be easily incorporated onto, or into, flexible/wearable substrates to provide superior performance along with reduction of cost.

Experimental

[0067] **Materials and Methods:** Polyethersulfone (PES) thin film was chosen as a flexible substrate due to its high mechanical, chemical and thermal stability. PES thin films of 500 μm thickness were obtained from Kmac (U.S). PES granules (3mm) with medium viscosity were obtained from Good fellow (U.K). All other chemicals were obtained from Sigma-Aldrich and used as received.

[0068] The PES granules were dissolved in dimethylformamide to a concentration of 26% (w/w) and electrospun membranes were fabricated with uniform diameter (583 ± 124 nm) and flawless morphology. VPP of PEDOT was performed on the PES substrates (2-D PES and 3-D PES) using procedures reported earlier.[19]

[0069] ZnO NWs were synthesized using seed mediated aqueous chemical growth.[21] Seed density was optimised to get full coverage on the PES substrates using scanning electron microscopy. The NWs were characterised using HR-SEM and HR-TEM.

[0070] To assess the suitability of the synthesized hybrid structures as NGs, sandwich structures were designed on different glass electrodes in order to avoid all noise and I-V characteristics were measured. ZnO NWs were grown on different substrates that were sandwiched to make a series of possible combinations of different junctions such as Au+ZnO-ITO, Au+ZnO-Au, Au+ZnO-PEDOT, ITO+ZnO-Au, ITO+ZnO-ITO, ITO+ZnO-PEDOT, PEDOT+ZnO-ITO, PEDOT+ZnO-Au and PEDOT+ZnO-PEDOT. (The '+' sign denotes the substrate on which the ZnO NWs were grown.)

[0071] The ITO-NGs were synthesized on commercially available flexible ITO coated PES. Current and voltage measurements were done using a Keithley 2612A sourcemeter. The flexing of NG was carried out using a tailor made set up. The measurements were carried out in a Faraday cage to isolate noise and external perturbations. Current and voltage generated by ITO-NG and PEDOT-NG was measured.

[0072] ZnO NWs grown on PEDOT functionalised 2-D PES were used as the bottom electrode and Au coated mylar was used as the top electrode. The two electrodes were sandwiched and stress was applied vertically using a tailor made set up. The flexing force was adjusted with a computer interface such that the travel speed of the flexing device was 0.41mm/s. For fibre NGs, ZnO NWs grown on PEDOT functionalized electrospun membranes (3-D PES) were sandwiched between ITO-PES and PEDOT-PES respectively. For linear integration a PEDOT functionalized PES fibre membrane was added between the sandwich structured fibre NG.

[0073] **Results and discussion:** PES in DMF (26% w/w) was electrospun with an applied potential of 1 kV/cm-1 to obtain uniform beadles of electrospun membranes with uniform diameter of 583 ± 124 nm. PEDOT was applied by VPP to 2-D and 3-D PES substrates. The success of PEDOT functionalisation was confirmed by the characteristic Raman peaks of PEDOT observed on functionalised substrate.

[0074] The observed peaks were very well matched with peaks reported in literature.[19]. A uniform thin layer of PEDOT was observed on SEM images 2-D PES and 3-D PES. ZnO NWs were synthesized using low temperature seed mediated growth method on PEDOT functionalized substrates. Seed density was optimized in terms of iterations of seed coating and dipping time to get complete surface coverage and vertically oriented NWs as shown in **Figure 1**.

[0075] The synthesized NWs were mesoporous, having a length of ~1500nm and grown in the (0001) direction with inter plane space separation was determined 0.26 nm. The corresponding SAED pattern showed wurtzite crystalline structure. The sheet resistance of the PEDOT coated 2-D PES was 94 Ω /square, measured using a four point probe. The sheet resistance was raised to 125 Ω /square after the ZnO NWs coating due to the highly alkaline growth medium, but the retained conductivity suggest that the ZnO NW growth did not affect the PEDOT on PES.[20]

[0076] Thus, n-type ZnO NES has been grown on p-type polymer (PEDOT) without compromising the stability of ZnO or the conductivity of the polymer. Consequently, it may be suitable to replace the ITO substrate from NGs of the prior art.

[0077] To test the feasibility of PEDOT+ZnO as a replacement for ITO+ZnO in NGs of the prior art, a simple measurement was attempted by creating sandwich structures similar to NGs without any applied force. Applying force was avoided because it has a tendency to modify the barrier height and junction properties. All the electrodes were fabricated on glass in order to increase the robustness and to avoid any vibrational perturbation. PEDOT+ZnO-Au and PEDOT+ZnO-PEDOT (**Figure 2c and 2d**) combination clearly demonstrate a p-n junction and the latter being understandably symmetric. Similar I-V curves was measured for the combinations of ITO+ZnO-Au and ITO+ZnO-PEDOT (**Figures 2a and 2b**) and these are comparable to what has been reported in the literature.[12,1]

[0078] Considering just the shape of the I-V curves, all four combinations show a rectification with a plateau before the reverse leakage current. The rectification demonstrates a p-n junction since the NW element is the same when two different electrodes are sandwiched at both the end of the NWs so arguably these structures

should act as an NG. This means that a VPP PEDOT electrode can form an ohmic contact (instead of an ITO) with ZnO NWs and can simultaneously act as a Schottky contact replacing Au (**Figure 2d**).

[0079] Although prior art theory generally teaches away from this proposal there are several examples in the literature of Au acting as both an ohmic and Schottky contact. The initial idea was to have one end acting as an ohmic contact using a material with less work function, but it was surprisingly found that when ZnO NWs are sandwiched between two gold contacts, the NG still worked. [22] The explanation offered was that one of the NW ends will act specifically as Schottky barrier and other will act as ohmic contact.

[0080] In principle a Schottky barrier is a p-n junction with comparatively small barrier height (0.6-0.8eV). A substrate that can act as both a Schottky barrier and an ohmic contact is surprising and not well understood, but it has been successfully demonstrated in devices such as piezoelectric diodes and laterally integrated NGs.[22]

[0081] Similarly, aluminium sheet has been used as both the top and bottom electrode, but significantly, an Al/In tip failed to generate any piezoelectric charges.[14,1] But in this example there was an additional insulating layer of PMMA that was been used between the top electrode and ZnO NWs in order to avoid leakage through metal-semiconductor junction using an infinitely high Schottky barrier. In other words a capacitance layer was inserted which helps Al to act as both a Schottky and an ohmic contact.

[0082] However there are examples such as gold and silver which forms both ohmic and Schottky contacts with ZnO, which vetoes the classification in accordance with work function suggesting intrinsic surface states, surface contamination/layers, inherent conductivity of the NWs prevail determining the electrical properties of the contacts.[23-26] When a piezopotential is induced across the interface it may lead to a linear tilt of the bands and Fermi level along the direction of the ZnO NWs which, in the case of the present invention, is in contact with a p-type polymer (similar to thermionic emission causes the changing the barrier heights).[27]

[0083] Since n-type ZnO NWs are grown on the top of p-type PEDOT, the immediate pacification of the free charge carriers in the ZnO to create a p-n junction will be much more dominant with less charge carriers available for screening piezopotential. The selective formation of an ohmic or Schottky contact at the PEDOT-ZnO interface is due to the formation of a p-n junction before flexing which causes the redistribution of energy barriers. It is worth noting that no insulating PMMA layer has been applied and no surface contaminations were observed at the PEDOT-ZnO interface.

[0084] Other possible combinations of substrates and top-electrodes were also tested and the I-V curves show different shapes without a rectification. The reverse combination of Au+ZnO-ITO junction does not show a rectification or Schottky barrier rather it forms an ohmic contact with top electrode showing the importance of directionality of junctions. Zhou et al explain that the Schottky barrier between ZnO and metals could be reversed and thus made to ohmic through piezoelectric polarization without changing interface structure or chemistry.[28] If the argument is true in all sense then the reverse combination of Au+ZnO-ITO should work as NG which is not true (when the force is applied vertically on the top electrode). But Au+ZnO-Au combination works because of the shape has a very small plateau with high reverse leakage current.

[0085] The direct explanations on offer will be the nonlinear rectification or antisymmetric effects on contacts with polar surface; these could explain the effect but not the directionality in the effect. In principle the Au+ZnO-PEDOT combination should work as NG according to the I-V curve but a considerable amount of noise was observed, shadowing the current and voltage outputs when this combination of NG was tested. (Note that the current scales different between combinations.)

[0086] In the light of the macroscopic I-V curves of sandwich structures, it is argued that if a sandwich structure is to function as an NG, it should have a rectifying top electrode for the ZnO NWs where the tensile force is applied. Without wishing to be bound by theory, this would explain how piezopotential can engineer the barrier height in order to turn one of the ends into ohmic and the other into Schottky by bending the Fermi levels, thus leading to better rectification. Moreover this argument is in line with a recent study of barrier height engineering using compressive strain and gating the transient flow of electrons (using a rectifying contact/Schottky) to split water [29]. The

junctions formed between ZnO and the top electrodes were usually assessed by a conductive contact mode AFM in order to study the energy harvesting properties.[1]

[0087] Piezopotential generated by an AFM gives the property of individual NWs rather than the NG as a whole; not the Fermi energy level differences of top and bottom electrode. The simple sandwich electrode studies reveals that when a ZnO sandwiched between two electrodes, the ZnO anchored electrode should form an ohmic contact with a rectified contact on the top to perform as a vertical NG.

[0088] **NG measurements:** Nanogenerators were made on flexible PES sheets and all the measurement were carried out with a custom build flexing device in a Faraday cage to avoid external perturbations. In order to compare the results and make sure that the piezoelectric current and voltage generated by the system were being measured, a comparison was made of the performance of PEDOT-NGs (**Figure 3**) with ITO –NGs (**Figure 4**).

[0089] The current measured using PEDOT NG was found to 10^6 times higher than ITO –NG (**see Figure 3**). The measurement was repeated for a number of cycles which gave a clear indication that the signal observed is due to piezoelectricity. The ITO-NG produced pico amperes of current and micro volts for a device of dimension 3cm × 1cm. ITO-NG shows a negative direct current (dc) as per reported in the literature [2] and the PEDOT-NG showed similar current pattern.

[0090] The speed of the flexing device was kept considerably low to avoid any enhancement of the signal to noise ratio. The possibility of misleading contributions from triboelectric charges was eliminated by measuring the blank electrode (without ZnO MWs). No significant charge generation was observed which confirms that the current and voltage generated is due to piezoelectricity.

[0091] The comparison was done with the ITO-NG and PEDOT-NG which were synthesized using low temperature solution grown techniques and the efficiency is compared to one on the other using in-house build device. When the device was flexed with higher speed, instead of increasing the current height a broader (more continuous) current peak was observed, which is evidence of PEDOTs capacitive ability.

[0092] **Suggested Mechanism of PEDOT+ZnO-Au and PEDOT+ZnO-PEDOT NGs:** When a force is applied to a piezoelectric crystal there will be a potential created in the crystal due to the relative displacement of cations and anions. In the case of semiconducting material such as ZnO the effective potential is screened by the charge carrier entity, that is, more charge carriers means less piezopotential.

[0093] A number of research groups have spin coated p-type conducting polymers such as P3HT and PEDOT:PSS on ZnO NWs in order to realise a p-n junction and hence reduce the free mobile charge carriers in the n type ZnO.[4,5] The major advantage of this study is to enhance the area of p-n junction, by growing n type ZnO on directly on p type PEDOT. The proposed mechanism is described in **Figure 5**.

[0094] **Figure 5(a)** shows a traditional ITO-NG, where there are two distinct junctions ITO-ZnO - an ohmic junction and Au-ZnO Schottky, so in this case a dc current and voltage is observed when a vertical stress is applied. Whereas in the case of PEDOT-NG, PEDOT+ZnO and ZnO+Au (or ZnO-PEDOT) junctions are Schottky but a dc current is still produced which is 10^6 times higher than ITO-NG system.

[0095] The sheet resistance of ITO coated PES is 50 Ω /square whereas PEDOT coated PES is 94 Ω /square, so the improved piezoelectric generation is not due to the lower resistance. In the case of PEDOT-NGs, there are two p-n junctions operating in tandem - a p-type hole conductor and an n-type ZnO and ZnO-metal (Au) Schottky contact. At the former interface holes from PEDOT have a tendency to diffuse in to ZnO NW region, and concomitantly, free electrons from ZnO diffuse into the PEDOT creating a charge depletion zone similar to a p-n Junction.[5] To describe this property, J.Briscoe et al proposed a screening model for ZnO-PEDOT: PSS which gives a relationship between electric field created by uncompensated charges (E_{dep}) and electric field produced against this by free carriers within the material or from external contact (E_{sc}) the summation of these electric field produce a net piezopotential on a crystal

$$E_{tot} = E_{dep} + E_{sc} \quad (5)$$

[0096] Without wishing to be bound by theory, the same argument may be extended to the present invention. Specifically, in PEDOT-NG, we have a higher contact area of

p-n junction and hence more charge depletion area. The speed of drift velocity for screening is quite slow due to the p type conduction through PEDOT which help to detect a high current and voltage output in the external circuit.

[0097] Contrary to all the cases in literature, in PEDOT-NG the bottom electrode is also Schottky, and this changes the performance quite drastically. In ITO-NG charges are accumulated at one end (ITO) when the force is applied vertically. If a similar scenario is considered for PEDOT-NG, due to the charge depletion area, electrons are pushed further away finding more holes in PEDOT-ZnO interface. On the other hand the electrons in the other end of a nanowire will be gated by the metal-semiconductor Schottky barrier at the Au interface. On extending the argument presented in K.Y. Lee et al [27] PEDOT-NG during flexing can be considered as three capacitors connected in series, that is, (i) PEDOT-ZnO, (ii) ZnO during bending, and (iii) ZnO-Au which results in a reduction of total capacitance, hence improve the output current and voltage generated. Since the current generated is dc, it is evident that one junction is rectifying the current, presumably the ZnO-Au interface. When electrons are pushed near to this interface due to the depletion, it act as gate to electrons (which help in accumulating more charge) and forward biasing with bending pushes the charges through the external circuit. So in summary, comparing with the prior art, the present invention includes synthesis a p-n junction dedicated to the screening of charges, by avoiding the use of ITO electrode. Here the junction and screening of charge carrier properties are found to be a more active player than electrode conductivity.

[0098] Following on from the encouraging results from the I-V testing of PEDOT+ZnO-PEDOT NGs were fabricated that exhibit the same performance as PEDOT+ZnO-Au and thus, allowing Au to be avoided. PEDOT+ZnO-PEDOT NG produces microamperes of current and microvolt voltage levels. This may be due the higher sheet resistance of the top electrode.

[0099] To compare the PEDOT+ZnO-Au with PEDOT+ZnO-PEDOT, the third capacitor (ZnO-Au) was been replaced with ZnO-PEDOT. Notably, PEDOT+ZnO-PEDOT-NG was not in conjunction with any supporting layer to avoid electron leakage. Instead ZnO-PEDOT was used to provide a well-defined p-n junction to gate the electrons.

[0100] A study was conducted to prove that top electrode will act as gate by a UV light assisted chrono-amperometry. In this study the conductivity of the bottom PEDOT+ZnO electrode was monitored while shining UV radiation from the top. ZnO is widely known as a photosensitive and photoconductive semiconductor that creates excitons when UV light is absorbed.[30] When hole electron pairs are created, the electrons are immediately injected into PEDOT which is evident by the immediate increase in resistance by almost 50% of its initial resistance, whereas pure PEDOT resistance remains unchanged. It is evident from this that the dragging force is due to the initially formed p-n junction, and it can be extended to an argument that ZnO NWs will have less number of screening charges at the top electrode. This indirectly means that there will be a great piezopotential created as in the cases of p-type ZnO.

[0101] ITO being a rigid surface is not ideal for NG. By contrast, PEDOT is a mechanically stable polymer, which helps the durability and statistical number of energy generating NWs. VPP polymerized/ oxidative chemical vapour deposited PEDOT does not show any visible microcrack formation and there is no reduction in the conductivity. In the case of ITO-NG, PMMA has been used to increase the robustness of the device, otherwise considerable reduction in the performance is observed. On the other hand PEDOT-NGs are durable for a few 100 cycles of measurements without any decrease in the performance and in addition p-type PEDOT screens the free carriers in electrons in the ZnO NWs.

[0102] **Fibre Nanogenerators:** To further develop the concept of a practical and wearable NG, ZnO NWs were grown on VPP polymerized PEDOT functionalized electrospun PES (3D-DPES) and tested as energy harvesting fibre membranes. PEDOT fibre-NG exhibited better performance when sandwiched between two PEDOT functionalized PES sheets instead of more conducting ITO sheets.

[0103] PEDOT fibre NG performs 10 times better when sandwiched between p-type PEDOT sheets thus reconfirming the mechanism suggested for PEDOT-NG. Attempts were made to linearly integrate the fibre NG by inserting a PEDOT functionalized electrospun membrane between two PEDOT fibre NGs, and the resultant current response was enhanced by more than 100 times. The direct current generation was due to the rectification offered by the PEDOT coated PES electrospun membrane. The

connection to the external circuit was made similar to PEDOT fibre-NG, so that positive half cycles will be rectified by the PEDOT electrospun which was not connected to the circuit.

[0104] While this invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification(s). This application is intended to cover any variations uses or adaptations of the invention following in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth.

[0105] As the present invention may be embodied in several forms without departing from the spirit of the essential characteristics of the invention, it should be understood that the above described embodiments are not to limit the present invention unless otherwise specified, but rather should be construed broadly within the spirit and scope of the invention as defined in the appended claims. The described embodiments are to be considered in all respects as illustrative only and not restrictive.

[0106] Various modifications and equivalent arrangements are intended to be included within the spirit and scope of the invention and appended claims. Therefore, the specific embodiments are to be understood to be illustrative of the many ways in which the principles of the present invention may be practiced. In the following claims, means-plus-function clauses are intended to cover structures as performing the defined function and not only structural equivalents, but also equivalent structures.

[0107] "Comprises/comprising" and "includes/including" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof. Thus, unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', 'includes', 'including' and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

References:

- [1] Wang, Z. L.; Song, J. H. *Science* 2006, 312, 242.
- [2] Wang, X. D.; Song, J. H.; Liu, J.; Wang, Z. L. *Science* 2007, 316, 102.
- [3] Kumar, B.; Kim, S. W. *J Mater Chem* 2011, 21, 18946.
- [4] Chung, S. Y.; Kim, S.; Lee, J. H.; Kim, K.; Kim, S. W.; Kang, C. Y.; Yoon, S. J.; Kim, Y. S. *Advanced materials* 2012, 24, 6022.
- [5] Briscoe, J.; Stewart, M.; Vopson, M.; Cain, M.; Weaver, P. M.; Dunn, S. *Adv Energy Mater* 2012, 2, 1261.
- [6] Choi, D.; Choi, M. Y.; Choi, W. M.; Shin, H. J.; Park, H. K.; Seo, J. S.; Park, J.; Yoon, S. M.; Chae, S. J.; Lee, Y. H.; Kim, S. W.; Choi, J. Y.; Lee, S. Y.; Kim, J. M. *Advanced materials* 2010, 22, 2187.
- [7] Choi, D.; Choi, M. Y.; Shin, H. J.; Yoon, S. M.; Seo, J. S.; Choi, J. Y.; Lee, S. Y.; Kim, J. M.; Kim, S. W. *J Phys Chem C* 2010, 114, 1379.
- [8] Bhattacharyya, D.; Howden, R. M.; Borrelli, D. C.; Gleason, K. K. *J Polym Sci Pol Phys* 2012, 50, 1329.
- [9] Jo, S. J.; Kim, C. S.; Kim, J. B.; Ryu, S. Y.; Noh, J. H.; Baik, H. K.; Kim, Y. S.; Lee, S. J. *Journal of Applied Physics* 2008, 103.
- [10] Zhou, J.; Xu, N. S.; Wang, Z. L. *Advanced materials* 2006, 18, 2432.
- [11] de Jong, M. P.; van IJzendoorn, L. J.; de Voigt, M. J. A. *Appl Phys Lett* 2000, 77, 2255.
- [12] Sharma, A.; Andersson, G.; Lewis, D. A. *Phys Chem Chem Phys* 2011, 13, 4381.

- [13] Shetty, A.; Nanda, K. K. Appl Phys Lett 2012, 100.
- [14] Riaz, M.; Song, J. H.; Nur, O.; Wang, Z. L.; Willander, M. Adv Funct Mater 2011, 21, 628.
- [15] Lee, S.; Hong, J. I.; Xu, C.; Lee, M.; Kim, D.; Lin, L.; Hwang, W.; Wang, Z. L. Advanced materials 2012, 24, 4398.
- [16] Barr, M. C.; Rowebl, J. A.; Lunt, R. R.; Xu, J. J.; Wang, A. N.; Boyce, C. M.; Im, S. G.; Bulovic, V.; Gleason, K. K. Advanced materials 2011, 23, 3500.
- [17] Hsu, J. W. P.; Tian, Z. R.; Simmons, N. C.; Matzke, C. M.; Voigt, J. A.; Liu, J. Nano letters 2005, 5, 83.
- [18] Zhang, Q. F.; Dandeneau, C. S.; Zhou, X. Y.; Cao, G. Z. Advanced materials 2009, 21, 4087.
- [19] Winther-Jensen, B.; West, K. Macromolecules 2004, 37, 4538.
- [20] Winther-Jensen, B.; Winther-Jensen, O.; Forsyth, M.; MacFarlane, D. R. Science 2008, 321, 671.
- [21] Greene, L. E.; Law, M.; Goldberger, J.; Kim, F.; Johnson, J. C.; Zhang, Y. F.; Saykally, R. J.; Yang, P. D. Angew Chem Int Edit 2003, 42, 3031.
- [22] Yang, R. S.; Qin, Y.; Dai, L. M.; Wang, Z. L. Nature nanotechnology 2009, 4, 34.
- [23] Chatman, S.; Ryan, B. J.; Poduska, K. M. Appl Phys Lett 2008, 92.
- [24] Liang, S.; Sheng, H.; Liu, Y.; Huo, Z.; Lu, Y.; Shen, H. J Cryst Growth 2001, 225, 110.

- [25] Wright, J. S.; Khanna, R.; Voss, L. F.; Stafford, L.; Gila, B. P.; Norton, D. P.; Pearton, S. J.; Wang, H. T.; Jang, S.; Anderson, T.; Chen, J. J.; Kang, B. S.; Ren, F.; Shen, H.; LaRoche, J. R.; Ip, K. *Appl Surf Sci* 2007, 253, 3766.
- [26] Mohammad, S. N. *Journal of Applied Physics* 2010, 108.
- [27] Lee, K. Y.; Kumar, B.; Seo, J. S.; Kim, K. H.; Sohn, J. I.; Cha, S. N.; Choi, D.; Wang, Z. L.; Kim, S. W. *Nano letters* 2012, 12, 1959.
- [28] Zhou, J.; Fei, P.; Gu, Y. D.; Mai, W. J.; Gao, Y. F.; Yang, R.; Bao, G.; Wang, Z. L. *Nano letters* 2008, 8, 3973.
- [29] Shi, J.; Starr, M. B.; Xiang, H.; Hara, Y.; Anderson, M. A.; Seo, J. H.; Ma, Z. Q.; Wang, X. D. *Nano letters* 2011, 11, 5587.
- [30] Keem, K.; Kim, H.; Kim, G. T.; Lee, J. S.; Min, B.; Cho, K.; Sung, M. Y.; Kim, S. *Appl Phys Lett* 2004, 84, 4376.
- [31] Hyunjin, K. et al., *Energy & Enviro. Sci.*, 2012, 1-8
- [32] Choi, M. Y. et al., *Adv. Mater.* 2009, 21, 2185-2189
- [33] Briscoe, J. et al, *Adv. Energy Mater.* 2012, pp. 1-8
- [34] Gao, P. et al., *Adv. Mater.* 2007, 19, pp.67-72
- [35] Yong Qin et al, *Nature* 2008, 451 doi:10.1038/nature06601

CLAIMS

1. A nanogenerator comprising a p-type conducting polymer substrate and a piezoelectric material.
2. A nanogenerator according to claim 1 wherein the p-type conducting polymer substrate is chosen from the group comprising polythiophenes
3. A nanogenerator according to claim 1 wherein the p-type conducting polymer substrate is poly(3,4-ethylenedioxythiophene).
4. A nanogenerator according to claim 1 wherein the piezoelectric material is chosen from the group comprising n-type semi-conductors, metals or combinations thereof.
5. A nanogenerator according to claim 1 wherein the piezoelectric material is zinc oxide
6. A nanogenerator according to claim 1 comprising a first electrode of polythiophene, and a second electrode of gold or polythiophene).
7. A method of manufacturing a nanogenerator according to claim 1 comprising the step of growing an n-type piezoelectric material directly on a p-type conducting polymer substrate.
8. A method of manufacturing according to claim 7 which includes a step of vapour phase synthesis.
9. A material comprising nanogenerators according to claim 1.
10. A material according to claim 9 wherein the material has at least one inner surface that comprises nanogenerators.
11. A material according to claim 9 which is a woven textile having warp and weft wherein the nanogenerators are incorporated into the warp or weft of the woven textile.

12. A material according to claim 9 which is non-porous.
13. A nanogenerator according to claim 1 adapted to power an electronic device.
14. A nanogenerator according to claim 1 when used to charge an electronic device.

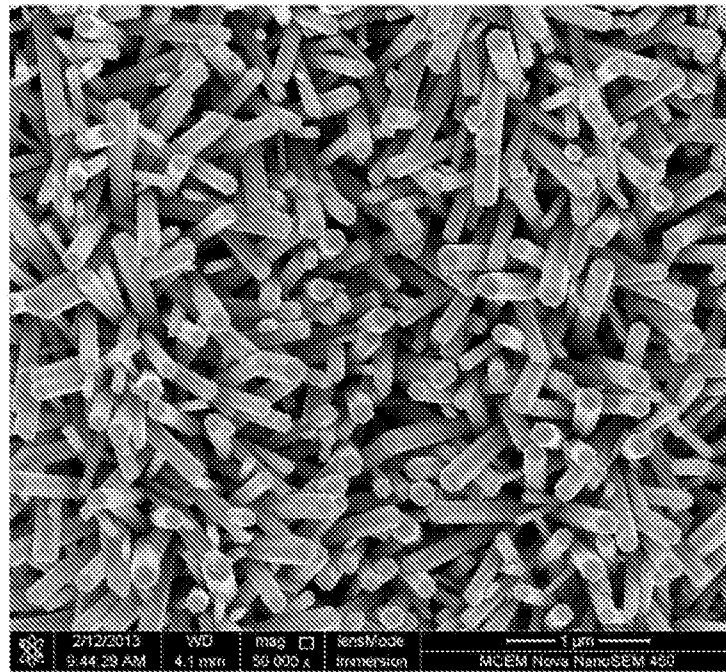


FIGURE 1

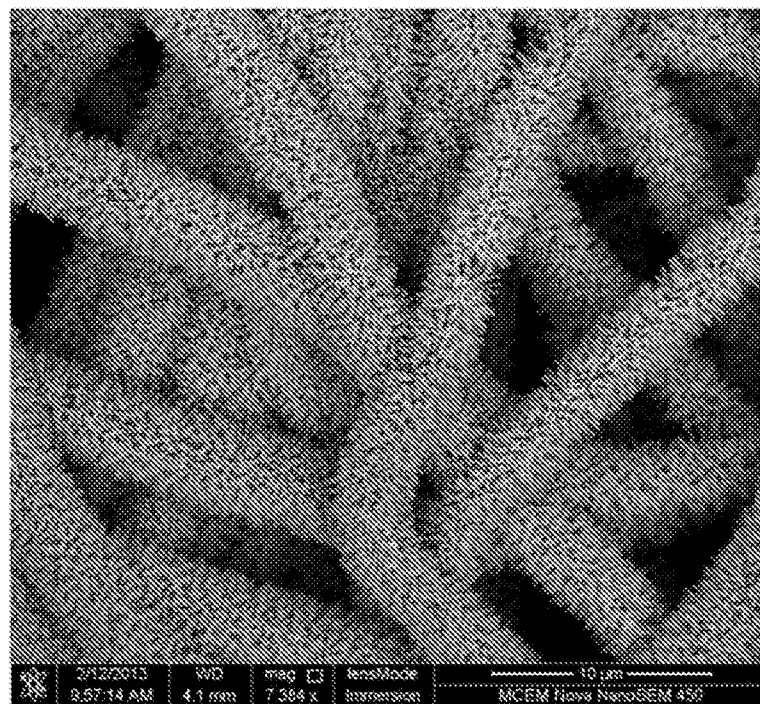


FIGURE 1(b)

2/9

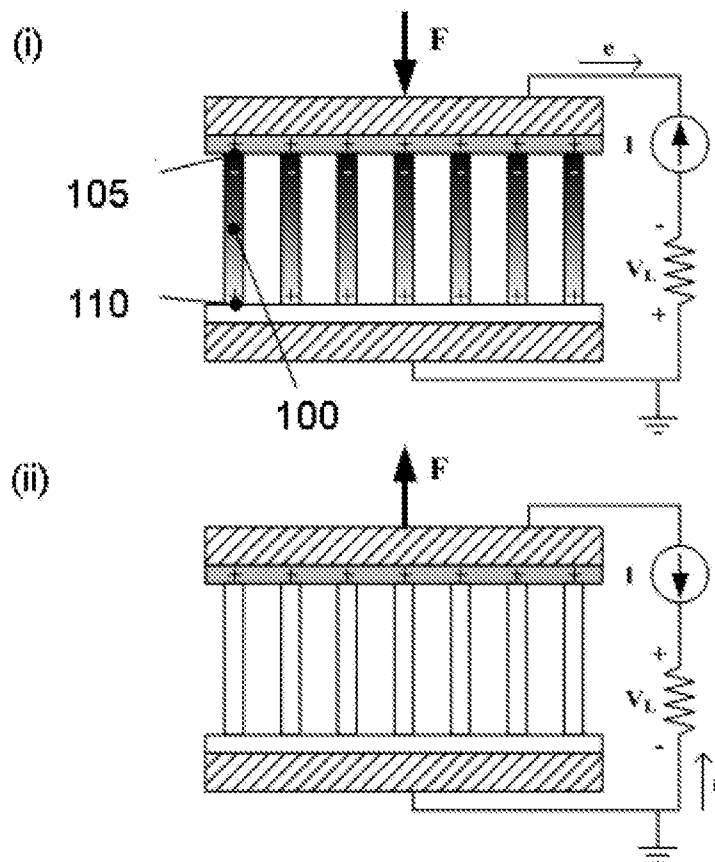


FIGURE 1(c)

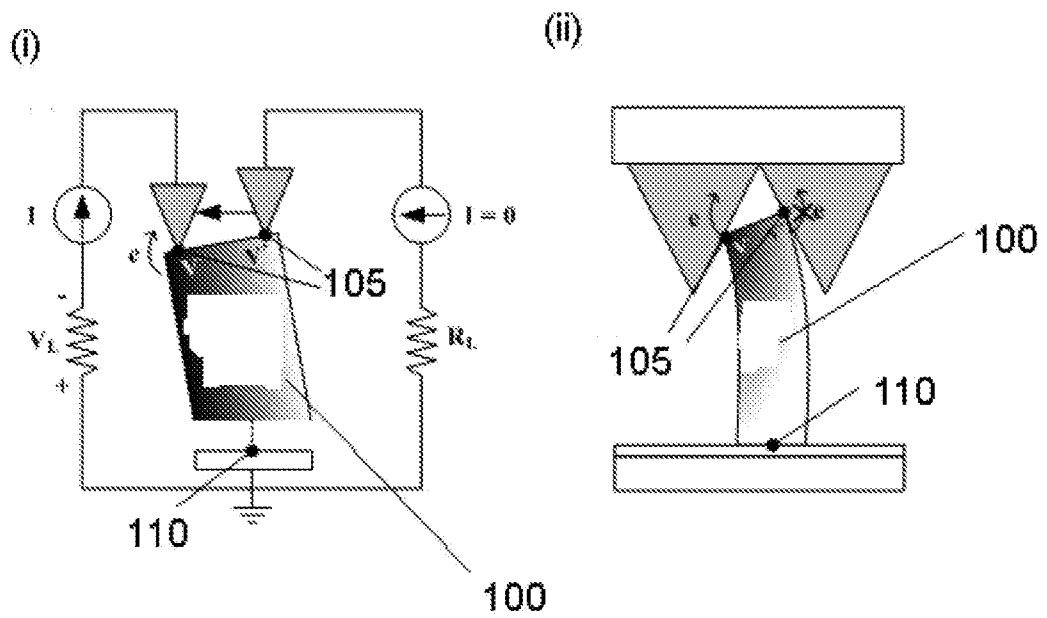
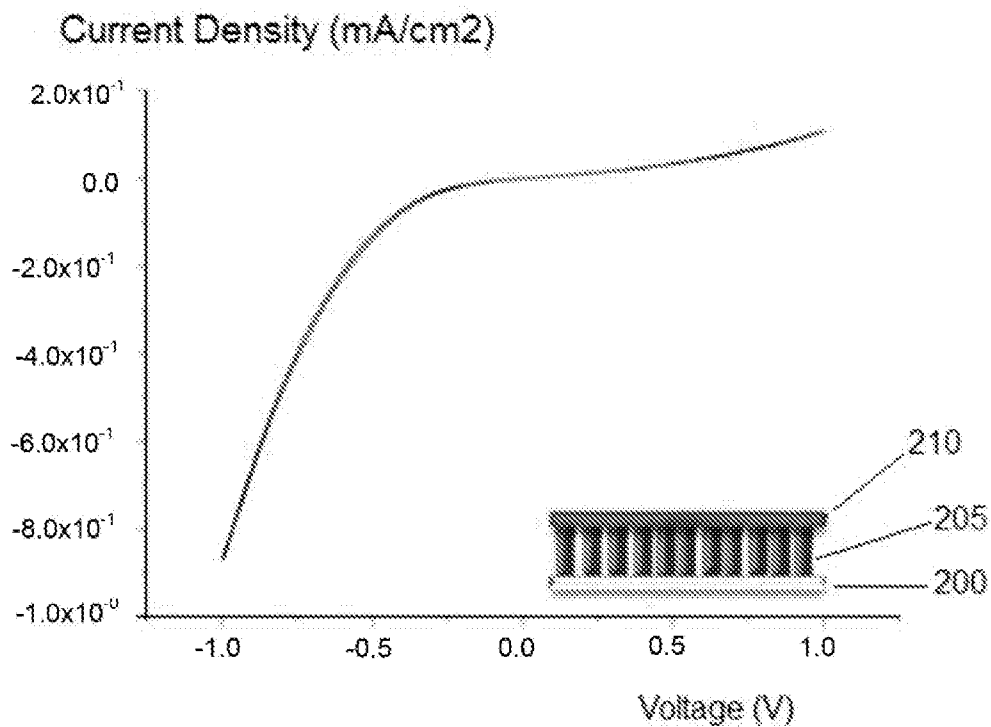
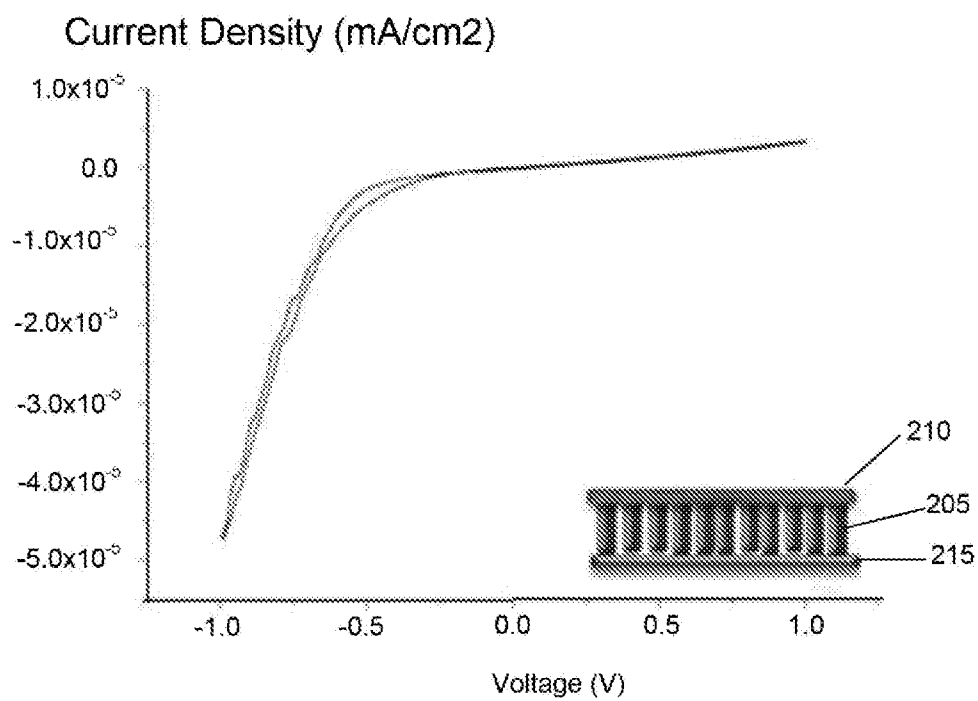
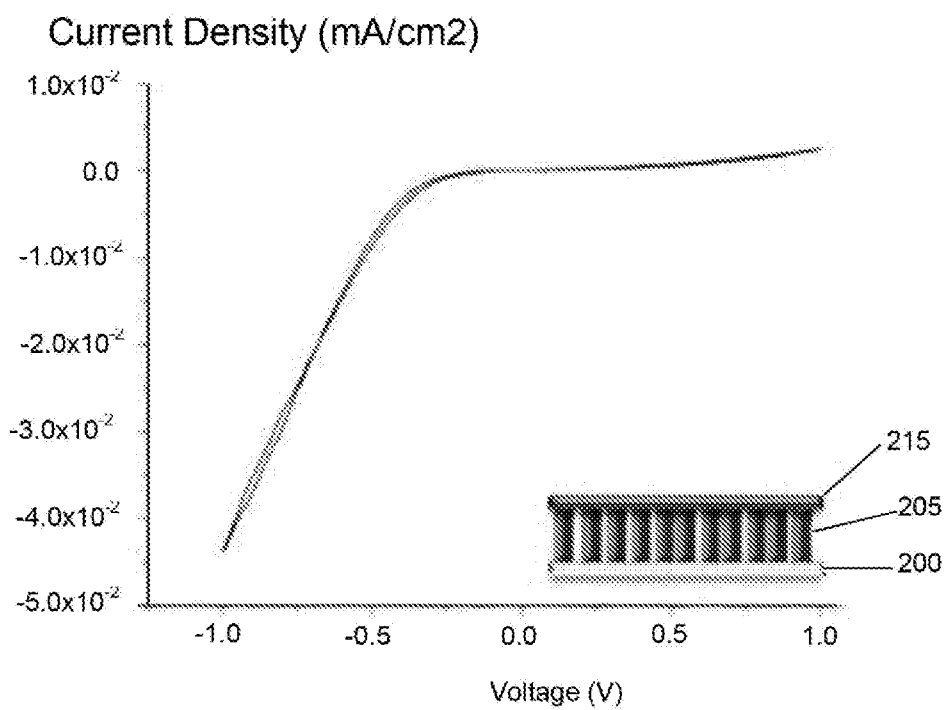
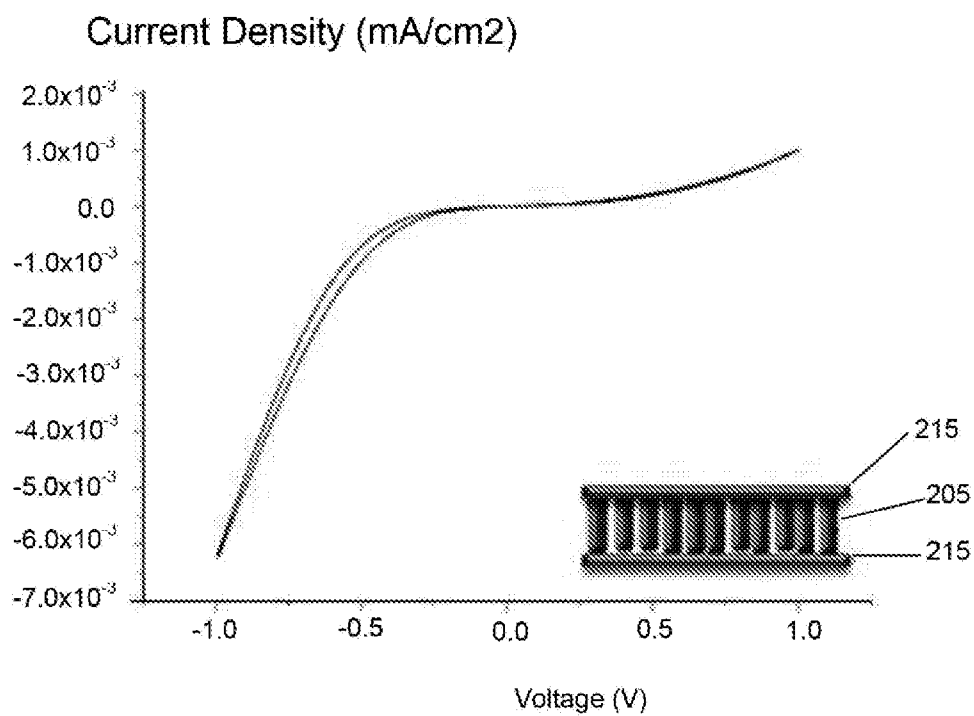


FIGURE 1(d)

**FIGURE 2(a)****FIGURE 2(b)**

**FIGURE 2(c)****FIGURE 2(d)**

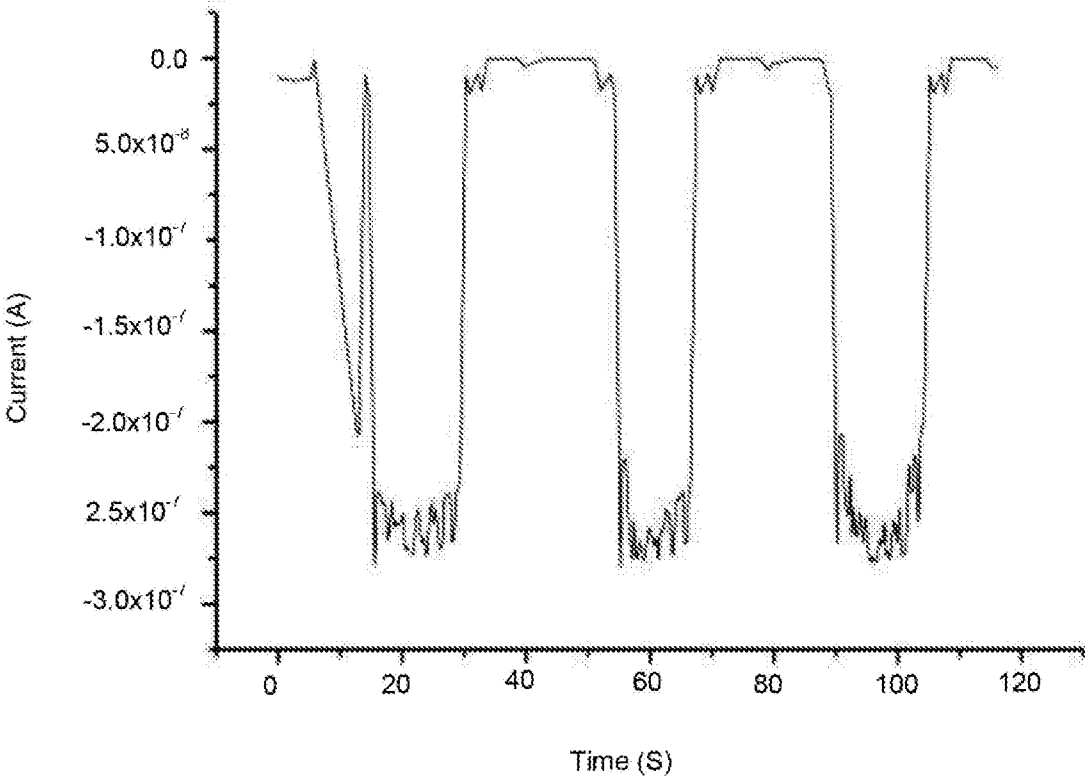


FIGURE 3(a)

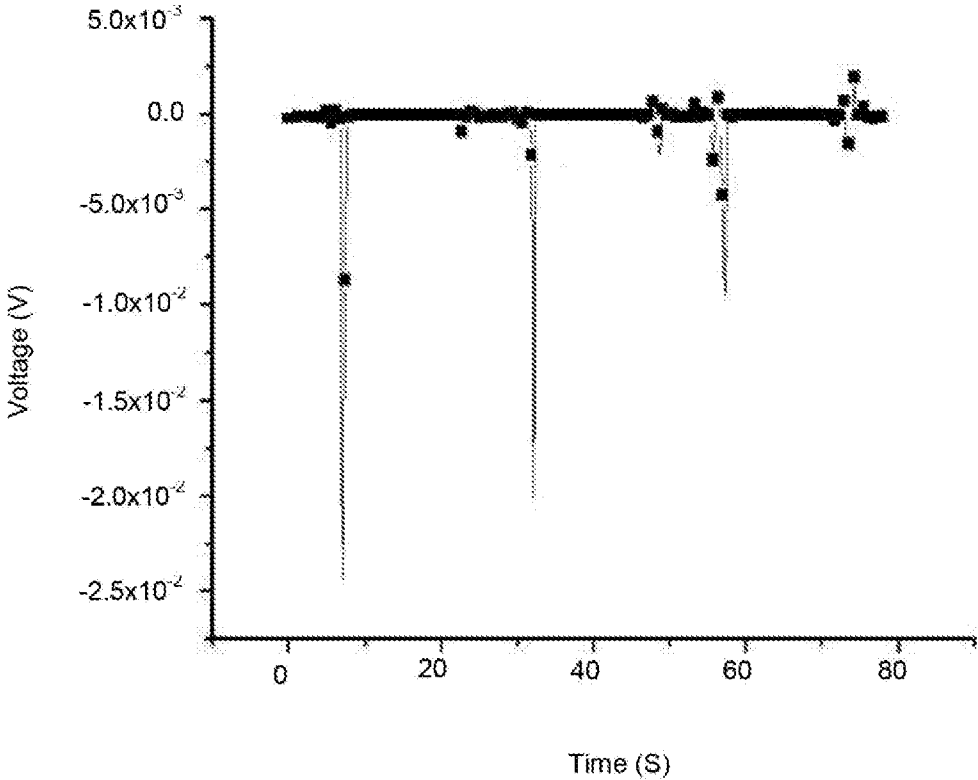
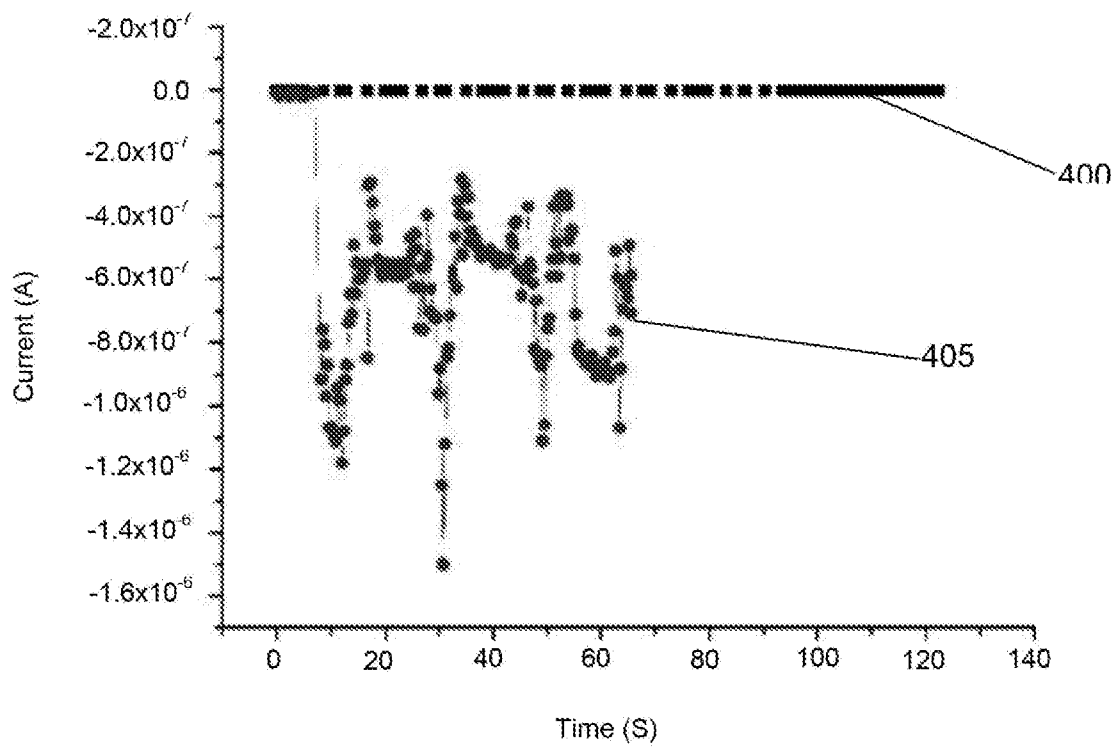
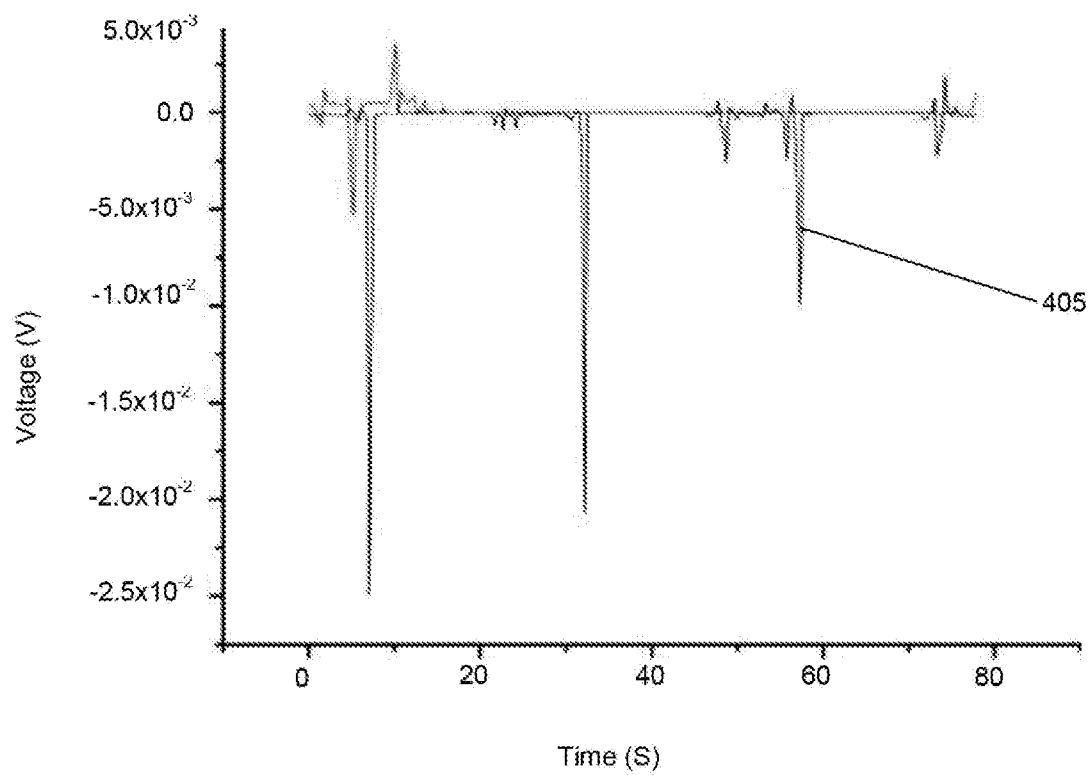


FIGURE 3(b)

6/9

**FIGURE 4(a)****FIGURE 4(b)**

7/9

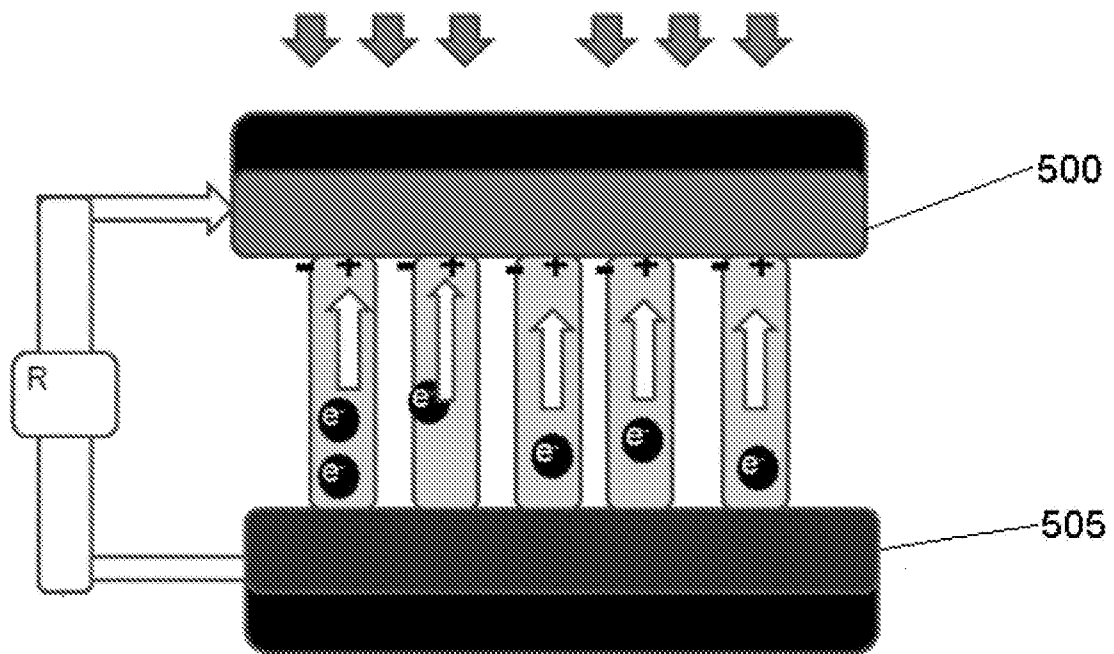


FIGURE 5(a)

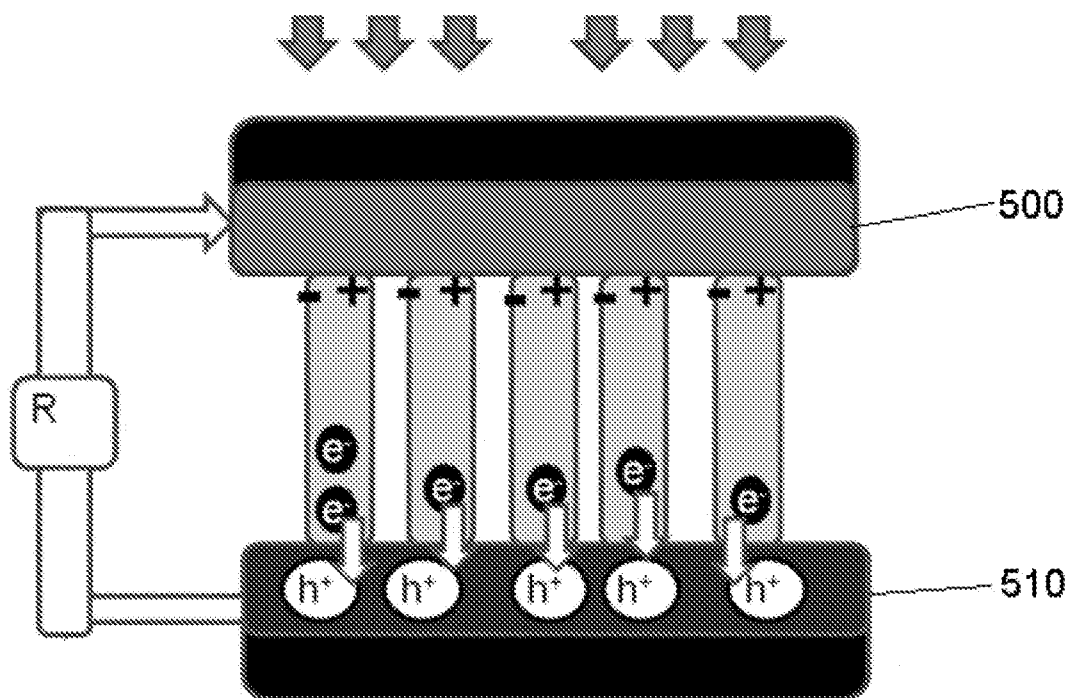


FIGURE 5(b)

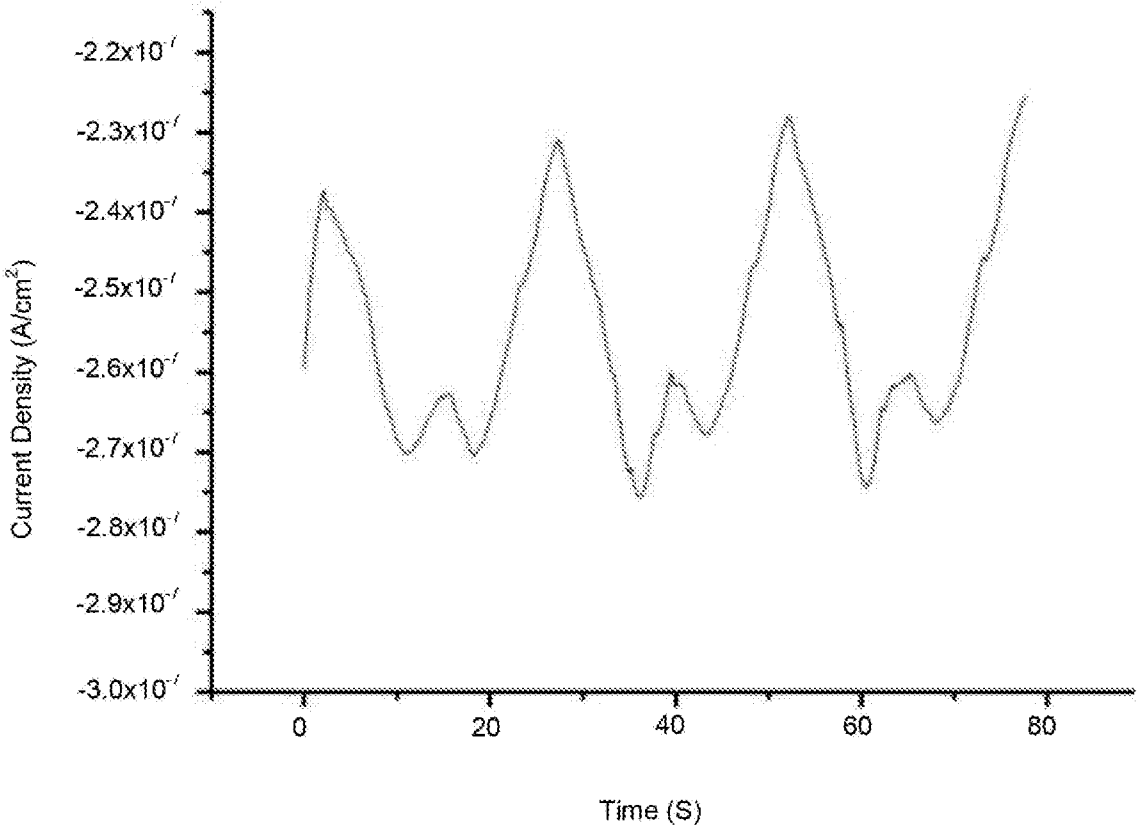


FIGURE 6(a)

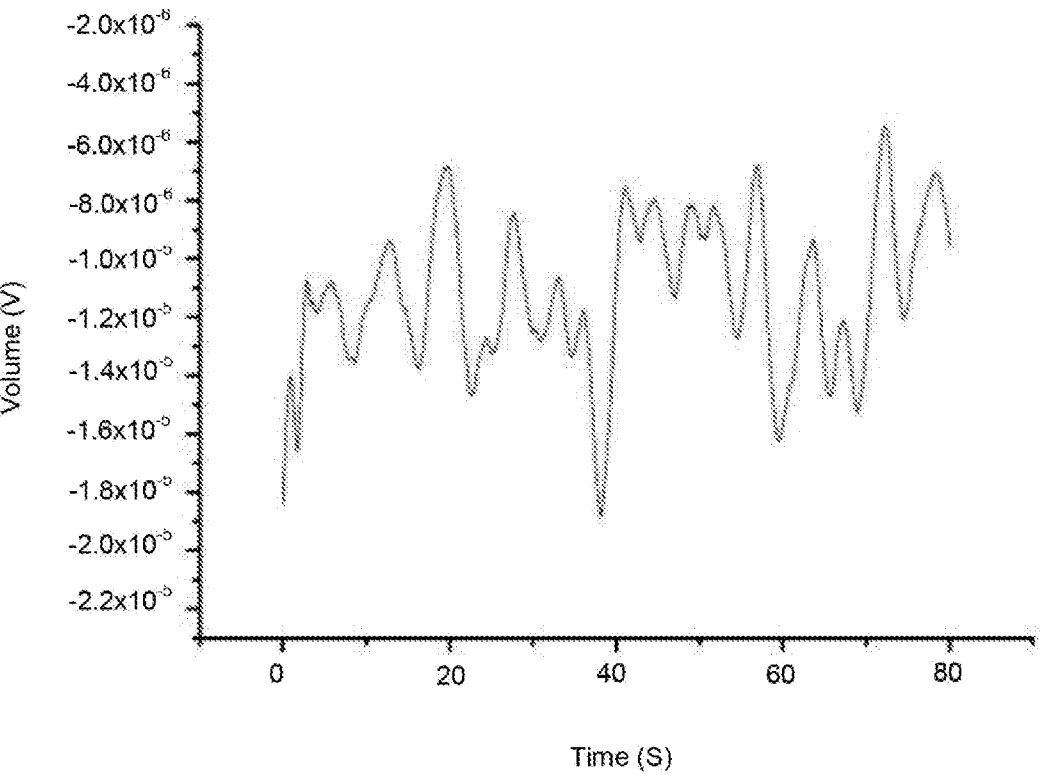


FIGURE 6(b)

9/9

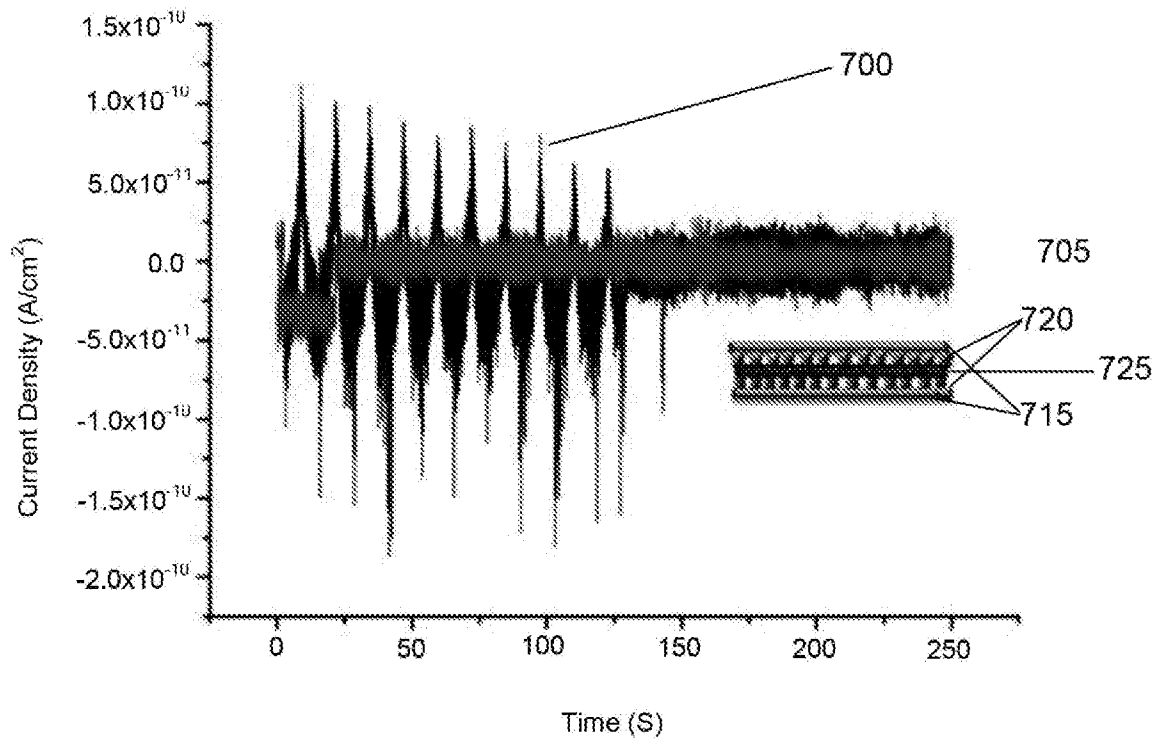


FIGURE 7(a)

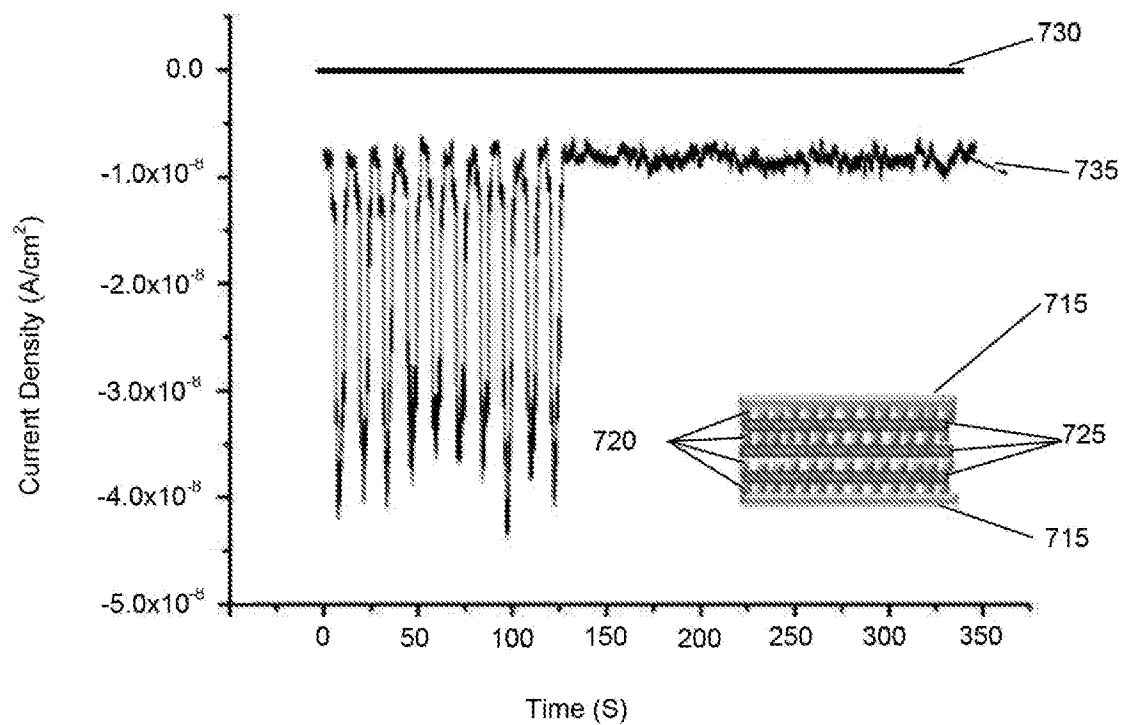


FIGURE 7(b)

A. CLASSIFICATION OF SUBJECT MATTER

H01L 41/113 (2006.01) H01L 41/053 (2006.01) H01L 41/18 (2006.01) H01L 41/31 (2013.01) H01L 51/00 (2006.01)
H02N 2/18 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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)

Databases: WPI and EPODOC. Keywords: H01L (CPC and IPC), B82B (CPC and IPC), B82Y (CPC and IPC), H02N2/-- (CPC and IPC), H04R17/-- (CPC and IPC), Y10S977/837 (CPC in EPODOC only), Y10S977/948 (CPC in EPODOC only), Y10S977/811 (CPC in EPODOC only); conducting polymer, polythiophene, ethylenedioxythiophene, PEDOT; piezoelectric, H01L41/-- (CPC and IPC); thermoelectric, pyroelectric, triboelectric; n-type semiconductor, metal, zinc oxide, ZnO; p-type; substrate, support, base, electrode; nanogenerator, self-powered; AND LIKE TERMS. Database: INSPEC. Keywords: conducting polymer, polythiophene, ethylenedioxythiophene, PEDOT; piezoelectric; thermoelectric, pyroelectric, triboelectric; n-type semiconductor, metal, zinc oxide, ZnO; p-type; substrate, support, base, electrode; nanogenerator, self-powered; Winther (Author), Nair (Author), Kolodziejczyk (Author) AND LIKE TERMS. Database: Espacenet. Keywords: Monash University as the applicant; Winther, Nair, Kolodziejczyk as the inventor; nanogenerator; piezo; energy scavenging, energy harvesting; polymer, polythiophene, ethylenedioxythiophene, PEDOT.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 20 October 2014	Date of mailing of the international search report 20 October 2014
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	Authorised officer Richard Baker AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832583

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2014/000789
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/0101315 A1 (CHOI et al.) 05 May 2011 Abstract, paragraphs 0009 to 0011, 0023 to 0097, figures 1A to 7	1-14
A	CHENG, Y.Y. et al., 'Development of flexible piezoelectric nanogenerator: Toward all wet chemical method', Microelectronic Engineering, 2011, vol. 88, p. 3015-3019, published online 1 May 2011. Whole document.	1-14
A	BRISCOE, J. et al., 'ZnO Nanogenerators - Energy Generation through Scavenging Vibration, Advantages of Using a Diode', Proceedings of SPIE 8763, Smart Sensors, Actuators, and MEMS VI, 2013, vol. 8763, p. 876308-1 to 876308-8, published 17 May 2013. Whole document.	1-14

Form PCT/ISA/210 (fifth sheet) (July 2009)

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2014/000789	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2011/0101315 A1	05 May 2011	US 8785914 B2	22 Jul 2014
		KR 20110047860 A	09 May 2011
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			