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Piezoelectric flexible nanogenerator based on ZnO nanosheet networks for mechanical energy harvesting

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ABSTRACT

Here, we report the simple and flexible nanogenerator based on ZnO nanosheet networks. ZnO nanosheets are synthesized by simple, cost-effective and single-step hydrothermal method on flexible conducting Aluminum substrates at a low growth temperature of 80 °C. Nanogenerator is fabricated using ZnO nanosheet networks as an active piezoelectric element with necessary electrodes. Fabricated nanogenerator tested under real-time mechanical forces such as finger tapping, muscle stretching, foot pressure, and mechanical bending. Nanogenerator output was verified by switching polarity and superposition tests and tests confirmed piezoelectric voltage. Fabricated nanogenerators produced open circuit voltage above 100 mV for the single device and 400 mV for four devices connected in series. The simplicity of this method and the reasonable output voltage of the cascaded nanogenerators are useful in practical energy harvesting for future needs.

1. Introduction

From the last decade, most of the research work has been focused on the sustainable and renewable energy sources such as solar, chemical, mechanical, thermal, wind, wave power energy, and also technologies designed to improve energy conversion efficiency [1–4]. In addition to the above, the availability of fossil fuels are limited and their usage produces the CO₂ and other gases into the atmosphere results in global warming [5]. Therefore, there is a need for producing clean, renewable and environmentally friendly alternate energy sources. Among all energy sources, mechanical energy is easily available in everywhere and all the time which is distinguished from other energy sources. Piezo and triboelectric technology mostly used for the conversion of mechanical energy into electrical energy. Triboelectric Nanogenerators were mostly reported for self-powered gas, flow, temperature sensors [6–11]. Piezoelectric technology is mostly used for converting mechanical energy into electrical energy in a simpler way. Piezoelectric thin films were used for mechanical energy conversion for the last few decades [12]. Thin films based energy harvesting system has certain disadvantages like large size, limited operating frequency, low output power, prone to cracks upon bending. Above said disadvantages overcome by designing the nanostructures based energy harvesting systems and it was named

as Nanogenerator [13].

From the last decade, nanostructures based nanogenerators are used for converting a variety of mechanical vibrations such as heartbeat, muscle stretching, eye blinking, limb movement, blood flow, wind flow, water flow, pressure, force, vibrations, etc into electrical energy [14,15]. ZnO nanorods are mostly used in piezo-electric nanogenerators in the literature [16,17]. The Piezo-electric voltage of few volts was observed with ZnO nanorods (Supplementary information (SI) S1). Growth of nanorods is a multistep process and it needs additional seed layer coating and annealing at higher temperatures. This multistep growth process becomes complex and expensive. Therefore, research is focused on a single step and simple growth process for ZnO nanostructures which can be used for nanogenerator fabrication. Recently, ZnO nanosheets are explored for the nanogenerator application with a single step growth procedure [18–20] (SI S2). However, very limited studies are there in the literature and there is a large scope for exploring the ZnO nanosheet based nanogenerators. Nanosheets have the advantage of more structurally stable under external load compared to the nanorods [18]. ZnO not only exhibits piezoelectricity also exhibits pyroelectricity, environmentally friendly and biologically compatible compared to other piezoelectric materials [21]. In this report, ZnO nanosheet networks used for the fabrication of nanogenerators are

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prepared at slightly lower growth temperature, with simple apparatus and also with different morphology compared to the literature reported ZnO nanosheets based nanogenerators [18–20] (SI S2). In this manuscript, flexible and conducting Aluminum foils were used as substrates for the growth of ZnO nanosheets. The main advantages of using Al substrate over other substrates such as ITO coated PET, ITO coated PES, ITO coated PEN and gold-coated PEN are (1) cost-effective, (2) ZnO nanosheets growth is directly obtained on Aluminum substrate without any additional seed layer deposition (or) surface treatment, (3) It acts as one conducting electrode for the nanogenerator device results in reduction of fabrication steps, (4) During nanosheets growth, ZnAl: layered double hydroxide (LDH) layer will be formed between Al substrate and ZnO nanosheets and this provides good adhesion of ZnO nanosheets to the substrate [18] (SI S3).

Here, we are reporting the nanogenerator made up of ZnO nanosheet networks prepared by simple solution synthesis onto a flexible conducting Aluminum substrate at a low growth temperature of 80°C without any extra seed layer deposition. It has shown excellent and reproducible piezoelectric output voltage.

2. Materials and methods

2.1. ZnO nanosheets synthesis

ZnO nanosheets were prepared by a single-step hydrothermal method similar to our previous report [22] and also literature [18]. Initially, Al substrates were cleaned with acetone, isopropanol, consequently de-ionized water for 10 min each in an ultrasonic cleaner and dried. ZnO nanosheets growth solution was prepared using Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and Hexamethylenetetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$) in equimolar ratio. Cleaned Aluminum substrates were placed over the growth solution and substrates were floating on the surface of the solution because of the surface tension. A small portion of all the substrates were covered with Kapton tape for the bottom electrode of the nanogenerator fabrication (SI S4). The glass beaker containing the growth solution and substrates was sealed with Aluminum foil and placed inside the hot air oven for about 4 h at the temperature of 80°C. Substrates were removed from the solution after 4 h of growth, rinsed with de-ionized water, and dried with blower (SI S4). Kapton tape removed substrates were used for further characterization and nanogenerator fabrication (SI S5).

2.2. Nanogenerator device fabrication and characterization

Nanogenerator was prepared by placing ITO coated PET substrate on to the ZnO nanosheets surface firmly without any short circuit and sealed with a Kapton tape leaving space for the electrode connections (SI S5). Two connecting cables were directly connected ITO coated PET substrate and Aluminum substrate. Digital Oscilloscope (GW-INSTEK GDS-1102-U) was interfaced to a computer with the help of Free wave software (version 3.23) for recording the generated open-circuit voltage of the nanogenerator in response to the applied mechanical force. Mechanical force on the nanogenerator was applied by finger tapping, bending, foot pressure, and muscle stretching. Prepared nanogenerator has also shown greater flexibility for the bending tests (SI S6).

3. Results and discussion

3.1. Characterization of ZnO nanosheets

Fig. 1(a)–(c) shows the morphology of the obtained ZnO nanosheets on the substrate at different magnifications. Inset of Fig. 1(b) shows the optical image of the ZnO nanosheets coated on an aluminum substrate and it is evident that ZnO coated region appears in white. Dense and porous nanosheets are observed all over the substrate. The cross-sectional SEM image is shown in Fig. 1(d) confirmed that the nanosheets

are in good contact with the Aluminum substrate and the height of the sheets are in the range of few microns. The cross-sectional image also confirms the formation interface layer ZnAl: LDH between ZnO nanosheets and Al foil. The formation of interface layer ZnAl: LDH between ZnO nanosheets and Al foil was confirmed previously in the literature also [18,22]. EDS spectrum collected on ZnO nanosheets is shown in Fig. 1(f). It shows the presence of Zn, O, and Al and confirms the purity of the ZnO nanosheets.

X-ray diffraction (XRD) pattern of the ZnO nanosheets is shown in Fig. 1(e). The intense diffraction peaks at 38.4°, 44.7° and 65.05° and 78.1° corresponds to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of the Al substrate. The diffraction peak at 34.5° is corresponding to the (0 0 2) plane of the ZnO confirm the formation of ZnO and the crystalline nature of the obtained ZnO nanosheets. The additional diffraction peaks at 33.7°, 60.1° corresponds to the planes of ZnAl:LDH. XRD diffraction also confirms the formation ZnAl:LDH at the interface of ZnO nanosheets and Aluminum.

3.2. Nanogenerator testing

To study the performance of fabricated nanogenerator, mechanical force is applied by tapping the finger against the nanogenerator and the response recorded with DSO interfaced with a computer. Fig. 2(a) shows the response of the nanogenerator for repeated finger tapping in the forward connection. The output voltage of 100–150 mV is produced for each finger tapping (SI Videos 1 and 2).

Fabricated nanogenerators on large area substrates are tested for the output voltage due to bending of the substrate, foot pressure and muscle stretching (SI Videos 3–5). Switching polarity test and superposition of voltage tests are conducted to confirm whether the generated output voltage is due to the piezoelectric effect or possible artifacts such as instrument noise suggested by the literature [23–26]. The output voltage produced by the Nanogenerator is due to the mechanical deformation of nanosheets by mechanical force. However, it is difficult to assign a mechanism for the production of voltage due to uncertainty in the polar axis of ZnO nanosheets [19].

In switching polarity test, the output voltage is measured by reversing the connections and the output voltage for each finger tapping is shown in Fig. 2(b). The output voltage in the reverse connections is the reversal of that obtained in the forward connection (SI Video 6). The switching polarity test confirmed that, generated output voltage coming from the nanogenerator device rather than the instrument noise [20,23,27,28]. Any noise signal generated from the measuring instrument will not change its sign from positive to negative when the connection is reversed. The superposition of the voltage test is conducted further to verify the measured output voltage by connecting nanogenerator devices in the same direction (series). When two nanogenerator devices are connected in the series the voltage of each nanogenerator is added to another one. The resulting output voltage will be sum of the individual nanogenerator voltages [23]. The forward connection of two nanogenerators is producing an output voltage in the range of ~200 mV which is shown in Fig. 2(e) (SI Video 7). Fig. 2(c) further confirms the addition of the output voltages when three nanogenerators are connected in the series. The output of the series connected three nanogenerator is in the range of ~300 mV which is thrice the individual nanogenerator voltage. Similarly, when four nanogenerators are connected in the same direction an output voltage of ~400 mV observed and is shown in Fig. 3(a). The real-time pictures of piezo-response testing by foot pressure, bending and muscle stretching are shown in Fig. 3(b)–(d).

The piezoelectric output generation mechanism of the proposed nanogenerator is similar to the mechanism proposed in the literature for ZnO nanosheets/nanorods based nanogenerators [20,28]. Piezoelectric output generation mechanism depends on the ZnO nanosheets deformation, formed ZnAl: LDH layer at the interface of ZnO nanosheets and Al substrate and Schottky barrier between ITO and ZnO

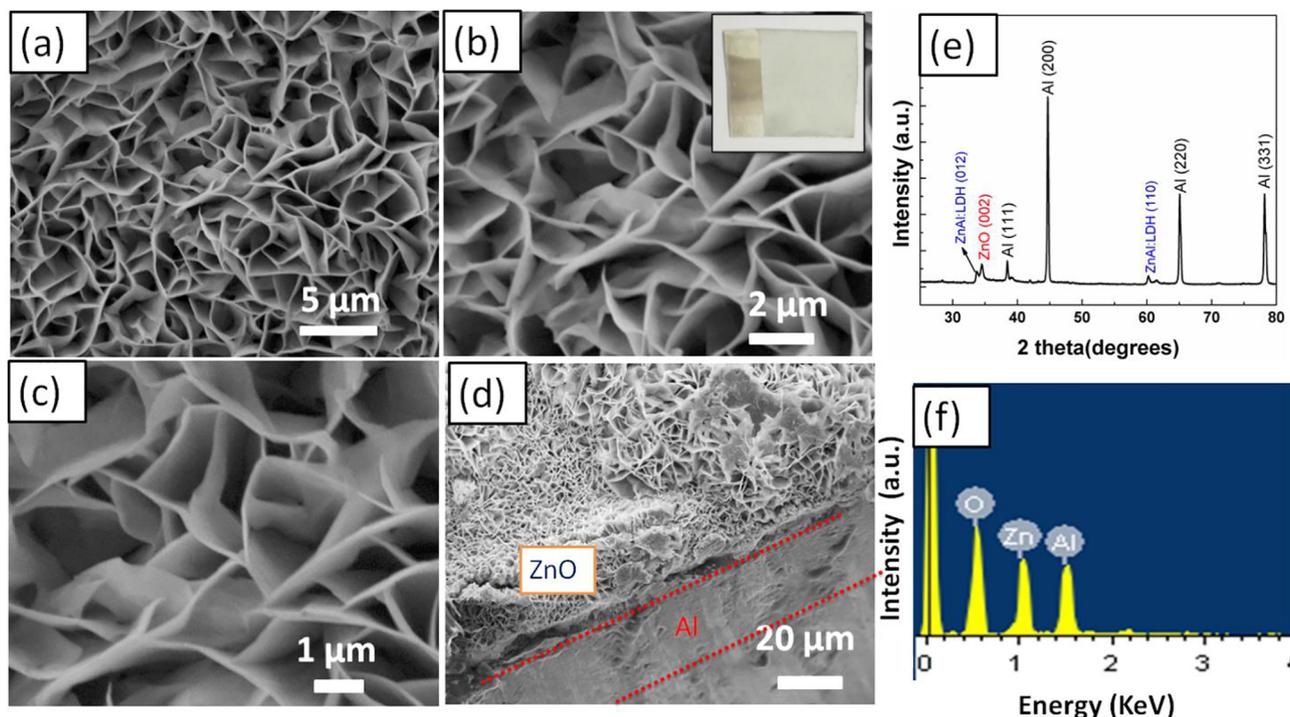


Fig. 1. (a)–(c) ZnO nanosheets SEM images at different magnifications, (d) cross sectional view of ZnO nanosheets on Al substrate (e) XRD pattern of the ZnO nanosheets, (f) EDS spectrum of the ZnO nanosheets grown on Al substrate.

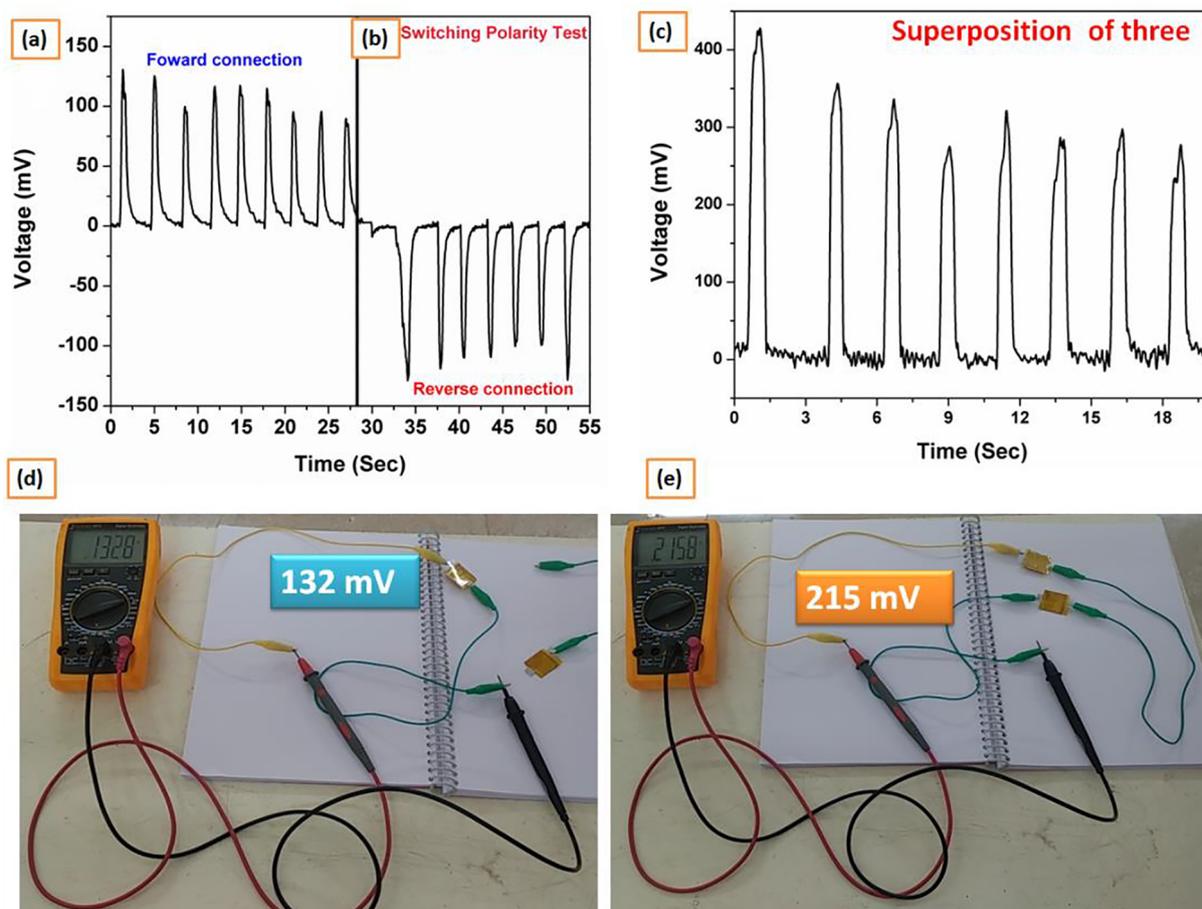


Fig. 2. Piezovoltage in response to finger tapping (a) forward connection, (b) reverse connection of single nanogenerator, (c) Series connection of three nanogenerators (d) Photograph of single nanogenerator connected to multimeter and its piezoresponse, (e) Photograph of series connected two nanogenerators to multimeter and its piezo-response.

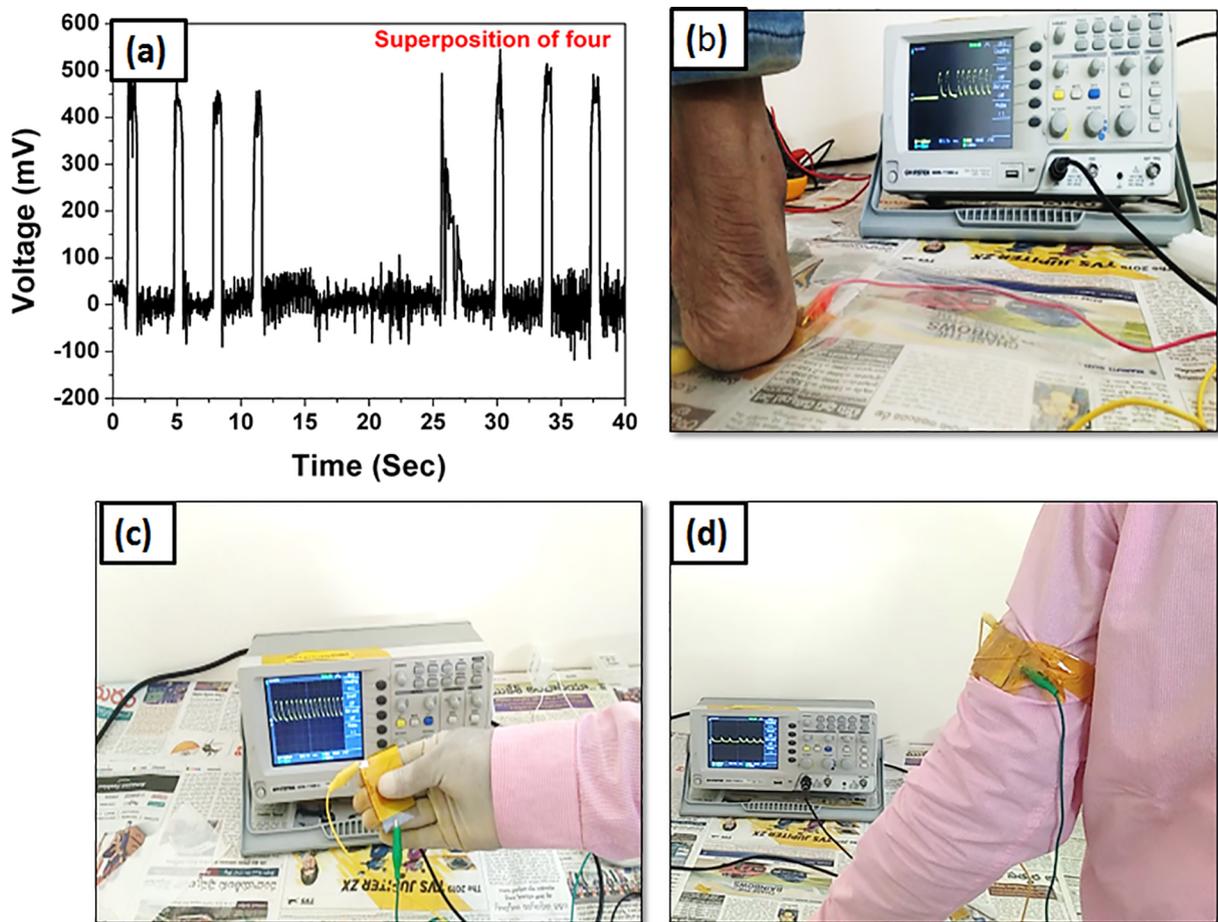


Fig. 3. (a) Piezoelectric output voltage of series connection of four nanogenerators, (b)–(d) real time photographs of the nanogenerator tested by foot pressure, bedning, muscle stretching respectively.

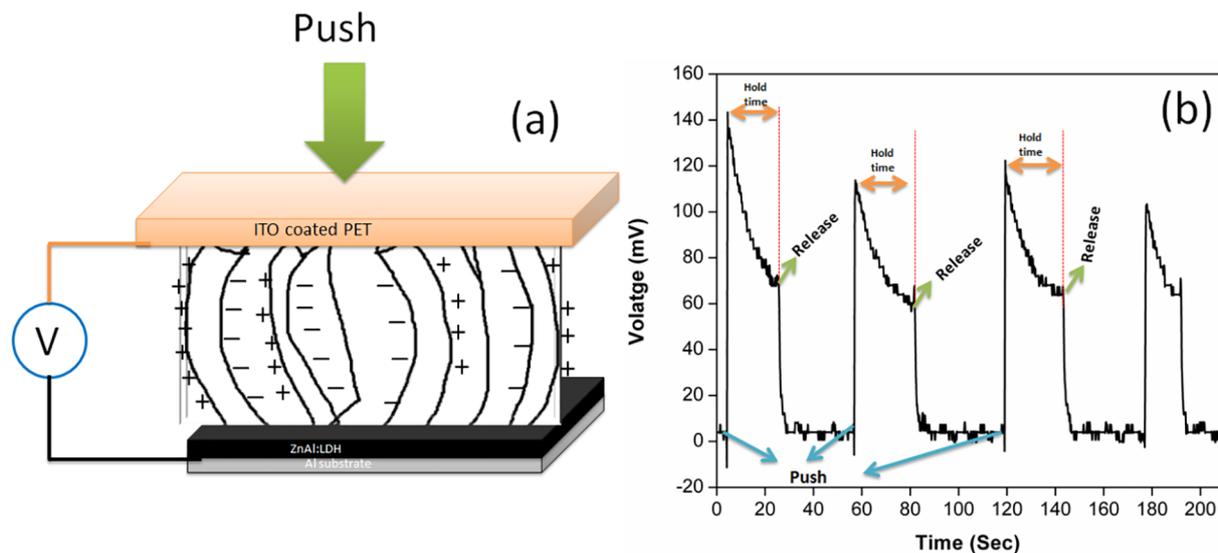


Fig. 4. (a) Proposed mechanism for the piezo voltage generation, (b) behavior of generated voltage pulses with the applied stress [28].

nanosheets. The ZnO nanosheets get buckled under applied force and generate piezo-potential in the ZnO nanosheets. The negative and positive potentials are induced in the compressed and stretched side of the nanosheets as shown in the Fig. 4(a) The Schottky contact formed between the ITO and ZnO helps in preserving the piezo-potential [28]. The generated piezo-potential induces the charges to store in the LDH

layer from ZnO nanosheets. The positive charges in the area of the LDH facing the nanosheets are compensated with free electrons from the ZnO nanosheets due to this negative charge build-up at the nanosheet/LDH interface. As a result of the above mechanism, strong potential difference developed and appeared as a voltage pulse in the measuring instrument [28].

The observed voltage pulse further analyzed with the behavior of the applied force like shown in Fig. 4(b). The rising part of the pulse is associated with piezo-potential generated due to the deformation of the nanosheets by the pushing force. No further rise in the piezo-potential when the applied force is held constant for some more time like shown in Fig. 4(b). When the applied force is held constant for further, the gradual decrease in the piezo-potential is observed. This decrease in the piezo potential is due to the generated positive piezo-potential at ZnO nanosheets which attracts electrons from the ITO electrode [28]. This gradual decrease in the voltage pulse takes place as long applied force held constant. However, the voltage pulse could not return to the original state perfectly as it was in the absence of the external force. This due to the small piezo potential still preserved in the holding time and could not be screened completely. Device output goes completely to the original state when the external force is removed [28].

The stability of the Nanogenerator was tested at different time intervals like immediately after the fabrication, after week, after a month and after 6 months. In all the cases, nanogenerator produced the same output voltage in response to the mechanical stress applied by a finger which indicates the good stability of the nanogenerator. Repeatability of the result was confirmed with testing of a large number of nanogenerator devices (~10) fabricated under identical conditions and all of them exhibited a similar responses to the applied stress. The output voltage obtained in this work can be further increased by the addition of more nanogenerators in the series.

4. Conclusions

In summary, a flexible piezoelectric nanogenerator was fabricated based on ZnO nanosheet networks. ZnO nanosheets were synthesized at a low growth temperature of 80 °C for a growth duration of 4 h by simple hydrothermal method. Fabricated nanogenerator was produced an open-circuit voltage of 100 mV upon finger tapping. Switching polarity test and superposition of voltage tests were conducted and confirmed the signals are coming from the nanogenerator devices rather than from the instrument noise. The output voltage obtained in this work can be further enhanced by the addition of more nanogenerators in the series. The high stability and repeatability of the Nanogenerators was confirmed at different time intervals and found high. The proposed nanogenerator can also be implemented as a self-power UV photodetector as fabrication of device involves transparent ITO electrode at the top of the ZnO nanosheets.

CRedit authorship contribution statement

Y. Manjula: Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualization. **R. Rakesh Kumar:** Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. **P. Missak Swarup Raju:** Funding acquisition, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. **G. Anil Kumar:** Data curation, Formal analysis, Investigation, Software. **T. Venkatappa Rao:** Writing - original draft, Writing - review & editing. **A. Akshaykranth:** Data curation, Formal analysis, Investigation. **P. Supraja:** Data curation, Formal analysis, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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