**ESKİŞEHİR TECHNICAL UNIVERSITY JOURNAL OF SCIENCE AND TECHNOLOGY A- APPLIED SCIENCES AND ENGINEERING**

**8th International Fiber and Polymer Research Symposium (8th ULPAS) - Special Issue 2021**

**2021, Vol.22 pp. 50-57, DOI:10.18038/estubtda.982143**

# WEARABLE TEXTILE-BASED PIEZOELECTRIC NANOGENERATORS WITH GRAPHENE/ZnO/AgNW

**Emre DEMİR [1], Ömer Faruk ÜNSAL [1], Filiz EMİROĞLU [2], Ayşe ÇELİK BEDELOĞLU [1,*]**

[1] Polymer Materials Engineering Department, Faculty of Engineering and Natural Sciences, Bursa Technical University, Bursa, Turkey
[2] Almaxtex (Yeşim) Tekstil San Tic A .Ş, Bursa Turkey

## ABSTRACT

In recent years, while people are dealing with problems such as global warming caused by environmental pollution caused by the use of traditional fossil energy sources, they have also faced the dilemma of energy crisis in the search for alternative renewable energy sources. The development of renewable and clean energy sources such as wind, solar and tidal energy has become increasingly important. In addition, nanogenerators, which convert waste mechanical energy into electrical energy through physical interaction, have attracted great interest among innovative studies in recent years. There is a need for maintenance-free and flexible wearable nanogenerators that can provide a sustainable power source for wearable/portable electronics. In this study, thermoplastic polyurethane (TPU) coated nanogenerator fabrics containing graphene / Zinc Oxide (ZnO) / Silver nanowires (AgNW) were developed for use in wearable electronics and the effect of zinc oxide concentration on the output power of textile-based nanogenerators was investigated. As a result, the nanogenerator fabricated using 7% by weight of ZnO produced 10 mW of power, indicating that ZnO-based materials can assist in the development of flexible TPU-based piezoelectric nanogenerators and advance to a new stage.

**Keywords:** Piezoelectric nanogenerator, Nanocomposite, Wearable electronic, Graphene, Textile electrode

## 1. INTRODUCTION

The use of fossil fuels for years along with the increasing energy demand has brought environmental problems, and the depletion of fossil fuels and their environmental damage has led to the concern of energy resources for the future. Driven by the latest technological advances and growing concerns about the environmental impact of the sustainability of traditional fuel usage, the possibility of generating significant amounts of clean, sustainable energy from renewable energy sources is of great interest worldwide for last a few decades. Solar, wind, biomass, and geothermal based energy sources are most known renewable energy sources [1]. It is stated that the global consumption of renewable energy sources will be reached a level equivalent to 318 exajoules (1 exajoule: 1 quintillion joules) of fossil fuels per year by 2050. This production rate also means that less than 0.01% of the 3.8 million exajoule solar energy reaching the earth's surface is used each year [2]. Moreover, there are studies that used two different energy conversion mechanisms in order to increase the energy conversion efficiency [3]. The conversion of small amounts of mechanical energy takes place between the vibrational and electrical forms of the material. The devices that convert small amounts of mechanical energy (or thermal) to electrical energy are named as nanogenerators [4]. The nanogenerators are divided into three main classes as pyroelectric nanogenerators that convert thermal energy into electrical energy, triboelectric nanogenerators and piezoelectric nanogenerators that convert mechanical energy into electrical energy [5]. Pyroelectric nanogenerators consist of thermally polarizable active layer and electrodes; thermally polarized active material generates the potential difference by a thermal gradient effect [6]. Triboelectric nanogenerators, based on static electrification between at least two different dielectric materials [7]. Finally, piezoelectric nanogenerators are devices that generate electrical energy under pressure or

*Corresponding Author: ayse.bedeloglu@btu.edu.tr
Received: 12.08.2021 Published: 30.11.2021

bending forces [8]. The nanogenerators convert human motion, water flow, rain droplets, wind, or vibration based mechanical energy into the electrical energy [9]. Wearable nanogenerators took remarkable attention for last five years in order to harvest human motion with textile comfort and low maintenance [10]. Wearable nanogenerators can be used for different purposes like health care sensors [11], energy harvesting [12], motion monitoring [13], human-machine interaction [14], and electronics [15]. Especially for wearable technologies, flexibility is one of the most studied points in engineering fields [16]. These devices can also be used as a power source for self-powered systems and reduce battery usage, which contributes to a reduction in environmental pollution in the long run.

ZnO, the well-known and cheapest piezoelectric material, is also a brittle, acid-soluble and white wurtzite crystal. ZnO nanowires was first time used as energy harvester in 2006 by Wang and then, nanogenerator concept was emerged. Wang produced vertically aligned ZnO nanowires on a polymeric substrate by chemical vapor deposition (CVD) method and The ZnO nano-forest produced electrical energy under the action of mechanical forces [9]. ZnO is also used by hybridizing with carbon-based materials for nanocomposite-based nanogenerator applications [17–20]. Chung et. al. used a thermoset polyurethane (PU) foam as substrate. PU foam was first coated with graphene oxide (GO) as bottom electrode and GO was reduced with ascorbic acid. Then, vertically aligned ZnO nanowires were grown by hydrothermal method. Finally thin Au film was coated onto nanogenerator as top electrode and nanogenerator generated 0.5 V voltage and 0.2 μA/cm2 current density [21]. In another work, ZnO nano-forest was grown on graphene-coated PET foil. ZnO-graphene layer was detached from PET substrate and other side of graphene was also coated with ZnO nanowires by hydrothermal method and ZnO/graphene/ZnO structure is obtained. Indium tin oxide (ITO) coated PET foils were used as top and bottom electrodes of the nanogenerator. Obtained piezoelectric nanogenerator generated 0.17 V voltage and 27.5 nA current [17]. Zhou group developed a highly stretchable energy generator based on thermoplastic polyurethane (TPU), silver nanowires (AgNW), reduced graphene oxide (rGO) and ZnO nanowires. This study demonstrated that AgNW and rGO has a synergistic effect to form electrically conductive pathway [10]. Besides, the ZnO nanomaterials, perovskite nanomaterials [22], polyvinylidene fluoride (PVDF) films [23], or nanofibers [24] can also be used as piezoelectric nanogenerators, while ZnO is more preferred due to its low cost and easy synthesis advantages.

In this study, the effect of ZnO nanowire concentration on the output voltage and current of textile-based nanogenerator devices was investigated. AgNW and rGO were used to form conductive pathways and transmit the generated electrical charge from the ZnO nanowires to the upper and lower electrodes. However, since the concentrations of AgNW and rGO in the nanocomposite will affect the output signals, the conductive filler concentrations were kept constant for each sample to clearly observe the effect of ZnO on the output signals. The prepared nanocomposite solutions were coated on a polyaniline-coated cotton fabric as the bottom electrode and coagulated on the fabric. The nanogenerators were fabricated by mounting the upper and lower electrodes on fabric samples. The nanogenerators were subjected to the bending test to simulate human elbow movement and output signals were recorded simultaneously.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Dimethyl formamide (DMF) (Merck) is used as solvent. Ether-based TPU was used as matrix polymer. Graphite powder(Merck), phosphoric acid (85% Sigma-Aldrich), sulfuric acid (98% Merck), hydrazine hydrate (55%, Sigma), hydrogen peroxide (35%, Sigma-Aldrich), hydrochloric acid (37%, Fischer Chemicals), and ethanol (ISOLAB) were used for rGO synthesis. Silver nitrate (99.5%, Sigma-Aldrich), polyvinylpyrrolidone (PVP), ethylene glycol (EG) (99.9% Sigma-Aldrich), and sodium chloride (NaCl) (99.9%, Sigma-Aldrich) were used for AgNW synthesis. Zinc nitrate hexahydrate, hexamethylene tetramine (HMTA) and ethanol were used for ZnO nanowire synthesis. Aniline (99.9%, Sigma-Aldrich),

hydrochloric acid (37%, WVR Chemicals) and ammonium persulfate (APS) (98%, Sigma) were used for polyaniline synthesis on fabric surface.

## 2.2. Methods

### 2.2.1. GO synthesis and chemical reduction

GO was synthesized according to Improved Hummers' Method [25]. 2 g of graphite powder was added into sulfuric acid-phosphoric acid mixture (9:1 by volume) and stirred for 30 minutes. After 30 minutes, 12 g of KMnO4 was added into flask and reaction was maintained overnight at 50 °C. Obtained brown mixture was poured onto 300 mL of deionized (DI) water ice in order to prevent sudden temperature rise. Then, 2 mL of H2O2 (30%) added in reaction mixture to neutralize the excess amount of KMnO4. Reaction mixture was centrifuged and brown GO powder was separated from liquid phase. GO flakes was washed with ethanol and HCl for once and washed with DI water for 20 times to removal of impurities. After washing step, GO was dried in fume hood for one week. GO powder was homogenized with ultrasonic homogenizator in DI water and reduced in 0.3 M hydrazine hydrate at 95 °C for 12 hours. Black rGO powder was washed with DMF for a few times to remove residual DI water and stored in DMF.

### 2.2.2. AgNW synthesis

AgNWs were synthesized with a modified method of literature [26]. Firstly, 0.007 g of NaCl was dissolved in 10 mL of EG. Separately, 0.204 g of AgNO3 was dissolved in 10 mL EG. 1 g of PVP was also separately dissolved in 20 mL of EG at 80 °C. NaCl solution was added slowly into the PVP solution. AgNO3 solution was also added dropwise to the reaction mixture. Heater was set to 180 °C and color change observed with increasing temperature (Figure 1). The color change is due to AgNO3-Ag transformation and Ag nanocube-Ag nanowire transformation [27]. The reaction mixture was cooled at room conditions. The AgNW dispersion was washed several times with acetone and DI water to remove PVP and ionic impurities. The final product was washed several times with DMF and stored in DMF.


**Figure 1.** Color change with increasing temperature in AgNW synthesis

### 2.2.3. ZnO nanowire synthesis

0.1 M of Zn(NO3)2.6H2O and 0,1 M HMTA solutions were mixed in equal volume [28]. Mixed solution was transferred in a PTFE lined hydrothermal reactor and heated to 180 °C for 8 hours. The reactor was cooled and white ZnO powder was washed with DI water and ethanol, respectively. Final powder was stored in DMF.

### 2.2.4. Polyaniline (PANI) coating of cotton fabric

PANI was synthesized by in-situ polymerization method [29]. with presence of woven cotton fabric. Molar ratio of aniline monomer and ammonium persulfate (initiator) was 4:1 and polymerization was performed in 1 M HCl solution. Firstly, Aniline-HCl solution was cooled in ice bath between 0-5 °C and cotton fabric was soaked in the solution. APS was dissolved in 1 M HCl solution and APS-HCl solution was added into monomer solution dropwise. Polymerization was maintained for 12 hours and PANI coated fabric was dried in an oven. Dried fabrics were doped with HCl fume.

### 2.2.5. Preparation of nanocomposite solutions

Each nanomaterial was stored in DMF, after synthesis steps and concentrations of each nanomaterial solution were determined by solvent removing method: Known volume of nanomaterial solution was heated up to 150 ˚C and residual solid was weighed with precision. All nanocomposite solutions contain 14% solid (polymer and additive) by weight. The concentration of conductive additives (rGO and AgNW) was 0.25% by weight in TPU. Nanomaterial concentrations were given in Table 1.

**Table 1.** Sample names and nanocomposite solution compounds

| Sample Name | ZnO (%) | AgNW (%) | rGO (%) |
|---|---|---|---|
| PNG1 | 1 | 0.25 | 0.25 |
| PNG2 | 3 | 0.25 | 0.25 |
| PNG3 | 5 | 0.25 | 0.25 |
| PNG4 | 7 | 0.25 | 0.25 |
| PNG5 | 9 | 0.25 | 0.25 |

### 2.2.6. Device fabrication

PANI coated fabrics were used as substrate of nanogenerators. Nanocomposite solutions were firstly poured onto fabrics and nanocomposite films were coated with a film applicator with thickness of 200 μm. The fabrics were immediately immersed in 1M HCl solution to coagulate the PU. HCl solution in coagulation bath prevented the dedoping of PANI in coagulation step due to ion impurity in water. The nanocomposite film-coated fabrics were sandwiched between two aluminum tapes, as the top and bottom electrodes. Sandwiched structure encapsulated with polydimethylsiloxane (PDMS) to mechanical stability and electrical insulation [30].

### 2.2.7.Characterization

The morphological analysis of AgNW and ZnO nanowires was performed by scanning electron microscopy (LEO GEMINI 1530, Carl Zeiss SEM) under 5 kV voltage with the distance between 8-9 mm. The electromechanical characterization was performed with a periodic bending apparatus designed

in our previous study [30]. The electrical contacts of nanogenerators were connected to an oscilloscope (GW INSTEK 1102-B) and output signals were recorded. A current clamp (FLUKE i30s) was also used for output current measurements. Output power values are calculated with Ohm's Law [31]:

$$P = V \times I \tag{1}$$

where P is power, V is open circuit voltage and I is short circuit current.

## 3. RESULTS AND DISCUSSION

### 3.1. SEM Results

SEM images of ZnO nanowires were given in Figure 2. ZnO nanowires have a diameter of about 130 nm and a length of 570 nm. As seen in the SEM images, several ZnO nanowires were grown on a nucleus [32]. SEM images also showed successful synthesis of AgNWs (Figure 3). The diameter distribution of AgNWs was very homogeneous and very thin (mean 23.6 nm) at 700 nm in length.

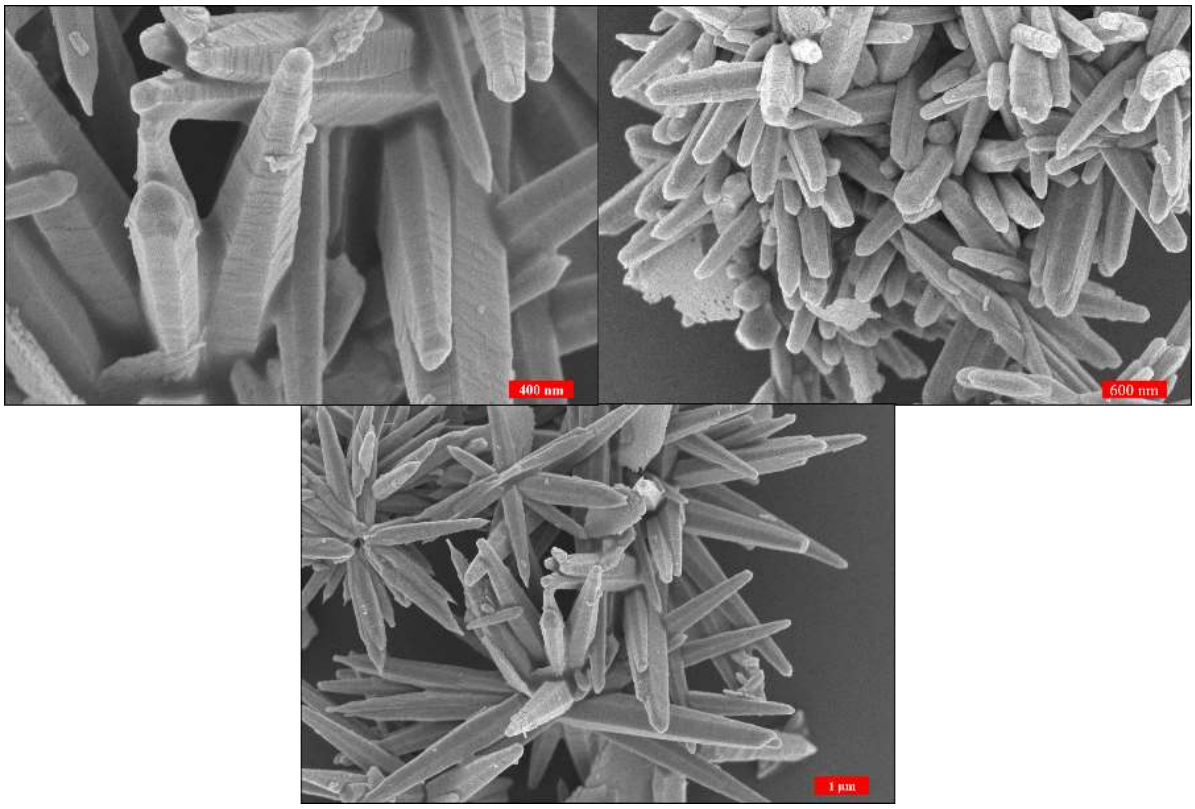


**Figure 2.** SEM images of ZnO nanowires

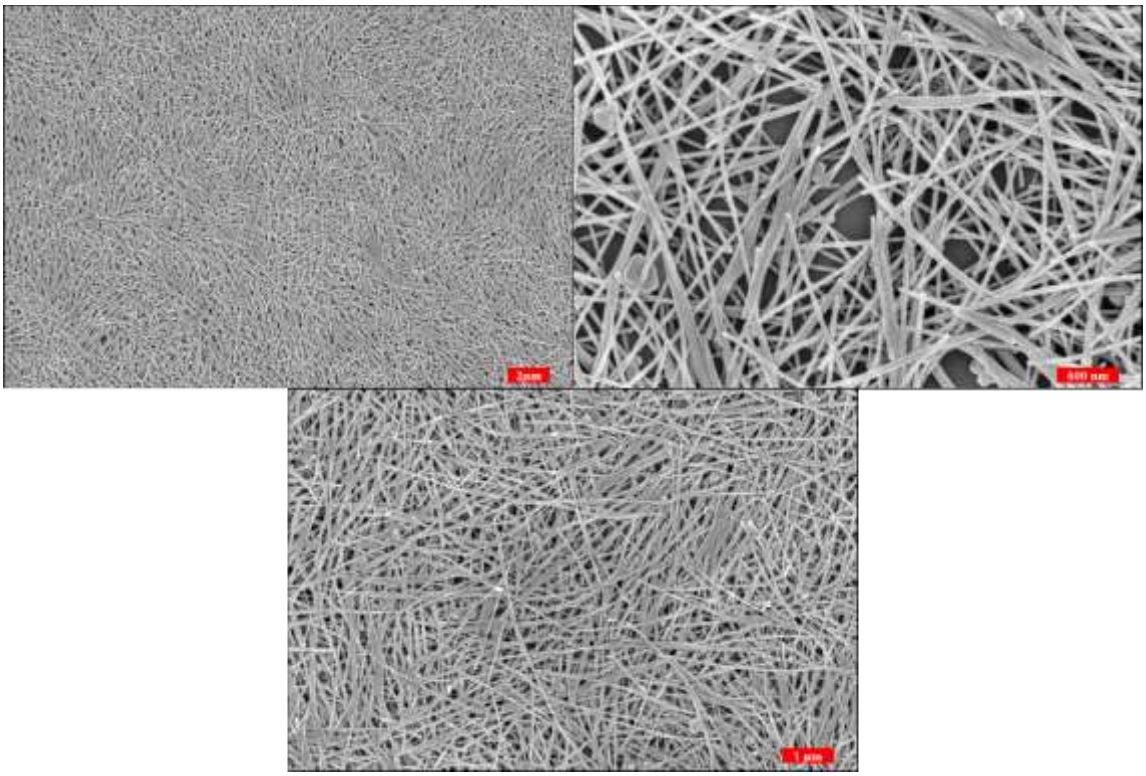

**Figure 3.** SEM images of AgNWs

### 3.2. Electromechanical Characterization

Piezoelectric energy conversion of all samples were monitorized with an oscilloscope. Every bending movement represented a peak in time-voltage graphs. Maximum signals were determined by Vp-p values. V-t graphs of nanogenerators were given in Figure 4. As a result of the voltage measurements, it was observed that the voltage signals increased with increasing The 9% ZnO doped nanogenerator showed lower piezoelectric output voltage than the 7% ZnO doped nanogenerator. On the other hand, the signal intensity increased up to the addition of 7% ZnO (Figure 4a-IV). The short-circuit current output signals were given in Figure 4b. All nanogenerators showed similar output current characteristics. However, a periodic signal (such as voltage graphs) could not be observed because the current produced was very low and not stable.

As a result of power calculations and P-t graphs, 7% ZnO doped nanogenerator showed the highest output power with 10.88 mW and the most intense signal output (Figure 4c-IV). Maximum output voltage, current and power values are also given in Figure 5. Maximum voltage and power values were obtained from 7% ZnO doped nanogenerator 1.12 V and 10.88 mW. The voltage and power values were increased with ZnO amount [33]. until 7% doping. It can be said that falling at 9% ZnO doping can be caused by increase on ZnO/conductive filler ratio with increasing ZnO amount. In other words, optimum ZnO/conductive ratio was 14 (7% ZnO doping, 0.25% graphene and 0.25% AgNW doping) for nanocomposite-based piezoelectric nanogenerators. The maximum output current as 72 mA was obtained from the 5% ZnO doped nanogenerator.

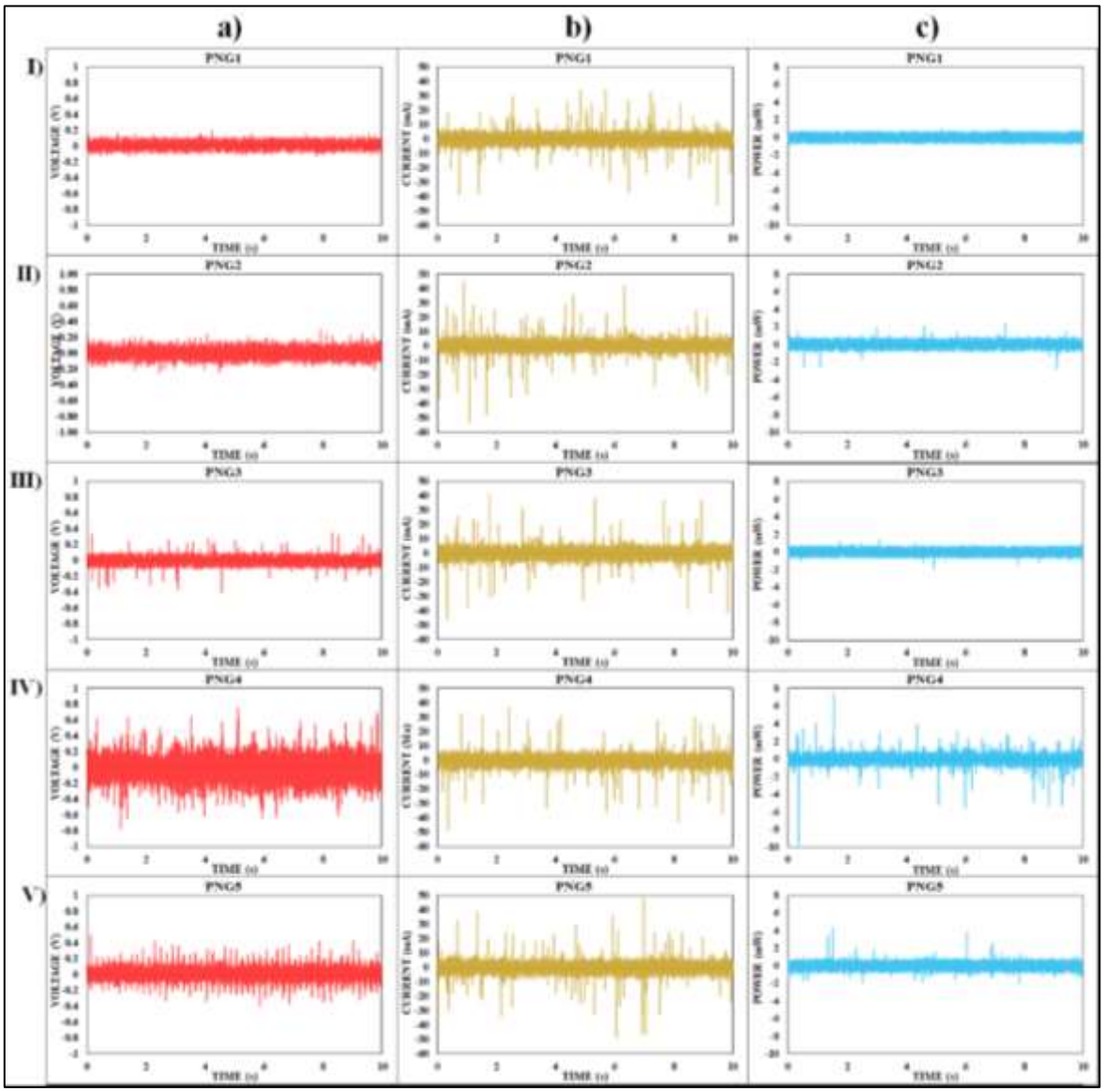


**Figure 4.** a) Voltage-time, b) current-time, and c) power-time graphs of piezoelectric nanogenerators

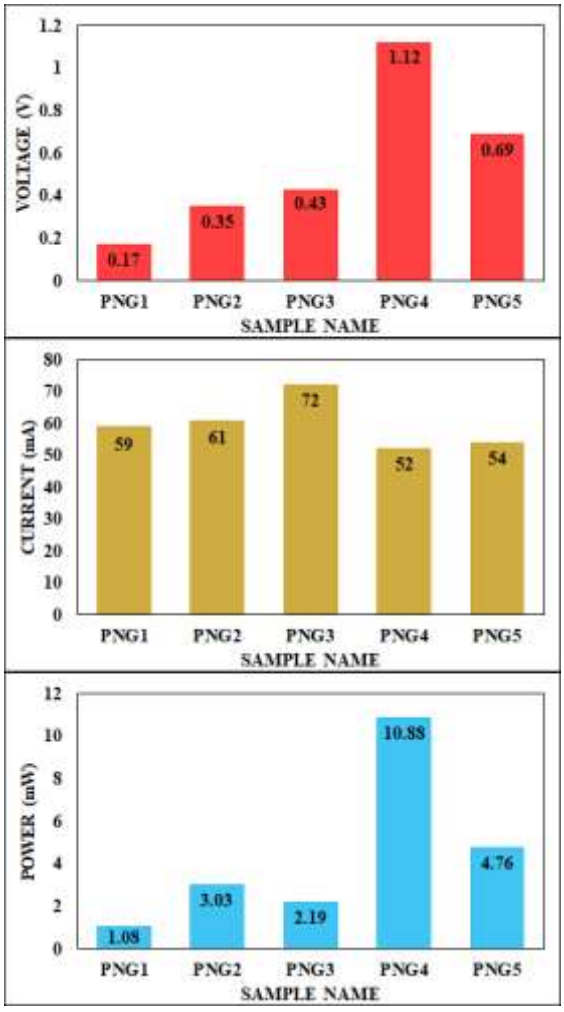


**Figure 5.** Maximum voltage, current and power output of nanogenerators

## 4. CONCLUSION

It has been observed that the amount of ZnO used in the produced nanogenerators generally increases in direct proportion to the energy conversion efficiency. According to the electromechanical results, it was observed that the PNG4 sample produced 1.12 V voltage and 52 mA current (the nanogenerator produced a total of 10 mW power). The energy conversion efficiency exhibited by the rGO/ZnO/AgNW doped samples showed that nanogenerators could be used by developing them with these materials. In addition, this study revealed the importance of the "piezoelectric material/conducting material" ratio for nanocomposite-based nanogenerators. It can be clearly seen that increasing the piezoelectric/conductor ratio improves the output signals up to a piezoelectric/conductor ratio of 14. However, above 14 output voltage and current signals started to decrease. Thanks to the sustainable features of nanogenerators, which are cleaner, renewable and environmentally friendly devices, it is predicted that they will take more place in human life in the future.

## ACKNOWLEDGEMENTS

This project was supported under the project application number 1139B411900326 within the scope of TUBITAK 2209-B Industry Oriented Undergraduate Research Projects Support Program.

## CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

## REFERENCES

[1] Commitment O U R, Strategy O U R, E. Use and E Management. Energy and Renewable Energy. 2014.

[2] Johansson T B, Kelly H, Reddy A K N, and Williams R H. Renewable energy: Sources for fuels and electricity. 1993

[3] Silva-Leon J, Cioncolini A, Nabawy M R A, Revell A, and Kennaugh A. Simultaneous wind and solar energy harvesting with inverted flags. Applied Energy, 239(February):2019; 846–858

[4] Bedeloğlu A, Ünsal Ö F, and Bedeloğlu A Ç. İletken Polimer Esaslı Nanojeneratörler. Afyon Kocatepe University Journal of Science and Engineering, 2018;18: 640–647

[5] Indira SS, Vaithilingam C A, Oruganti K S P, Mohd F, and Rahman S. Nanogenerators as a sustainable power source: state of art, applications, and challenges 2019

[6] Xue H, Yang Q, Wang D, Luo W, Wang W, Lin M, Liang D, and Luo Q. A wearable pyroelectric nanogenerator and self-powered breathing sensor. Nano Energy, 2017; 38(May): 147–154

[7] Wang Y, Yang Y, and Wang Z L. Triboelectric nanogenerators as flexible power sources. Npj Flexible Electronics, 2017; 1(1): 1–9

[8] Fan F R, Lin L, Zhu G, Wu W, Zhang R, and Wang Z L. Transparent triboelectric nanogenerators and self-powered pressure sensors based on micropatterned plastic films. Nano Letters, 2012; 12(6): 3109–3114

[9] Wang Z L and Song J. Piezoelectric nanogenerators based on zinc oxide nanowire arrays. Science, 2006; 312(5771): 242–246

[10] Zhou K, Zhao Y, Sun X, Yuan Z, Zheng G, Dai K, Mi L, Pan C, Liu C, and Shen C. Ultra-stretchable triboelectric nanogenerator as high-sensitive and self-powered electronic skins for energy harvesting and tactile sensing. Nano Energy, 2020; 70(January): 104546

[11] Wang L and Daoud W A. Hybrid conductive hydrogels for washable human motion energy harvester and self-powered temperature-stress dual sensor. Nano Energy, 2019; 66(July): 104080

[12] Lu L, Ding W, Liu J, and Yang B. Flexible PVDF based piezoelectric nanogenerators. Nano Energy, 2020; 78(July): 105251

[13] Liu Z, Zhang S, Jin Y M, Ouyang H, Zou Y, Wang X X, Xie L X, and Li Z. Flexible Piezoelectric

Nanogenerator for Wearable Self-powered Respiration Active Sensor and Healthcare Monitoring. Materials Research Express, 2019; 0–12

[14] He X, Zi Y, Yu H, Zhang S L, Wang J, Ding W, Zou H, Zhang W, Lu C, and Wang Z L. An ultrathin paper-based self-powered system for portable electronics and wireless human-machine interaction. Nano Energy, 2017; 39(April): 328–336

[15] Feng X, Zhang Y, Kang L, Wang L, Duan C, Yin K, Pang J, and Wang K. Integrated energy storage system based on triboelectric nanogenerator in electronic devices. Frontiers of Chemical Science and Engineering, 2021; 15(2): 238–250

[16] Dong K, Peng X, and Wang Z L. Fiber/Fabric-Based Piezoelectric and Triboelectric Nanogenerators for Flexible/Stretchable and Wearable Electronics and Artificial Intelligence. Advanced Materials, 2020;32(5): 1–43

[17] Shin D M, Tsege E L, Kang S H, Seung W, Kim S W, Kim H K, Hong S W, and Hwang Y H. Freestanding ZnO nanorod/graphene/ZnO nanorod epitaxial double heterostructure for improved piezoelectric nanogenerators. Nano Energy, 2015; 12: 268–277

[18] Lin L, Hu Y, Xu C, Zhang Y, Zhang R, Wen X, and Lin Wang Z. Transparent flexible nanogenerator as self-powered sensor for transportation monitoring. Nano Energy, 2013; 2(1): 75–81

[19] Cherumannil Karumuthil S, Rajeev S P, and Varghese S. Piezo-tribo nanoenergy harvester using hybrid polydimethyl siloxane based nanocomposite. Nano Energy, 2017; 40(August): 487–494

[20] Li X, Chen Y, Kumar A, Mahmoud A, Nychka J A, and Chung H J. Sponge-Templated Macroporous Graphene Network for Piezoelectric ZnO Nanogenerator. ACS Applied Materials and Interfaces, 2015; 7(37): 20753–20760

[21] Yilmaz Y and P. Mazumder P. A drift-tolerant read/write scheme for multilevel memristor memory. IEEE Transactions on Nanotechnology 2017; 16(6): 1016–1027

[22] Kandpal M, Palaparthy V, Tiwary N, and Rao V R. Low Cost, Large Area, Flexible Graphene Nanocomposite Films for Energy Harvesting Applications. IEEE Transactions on Nanotechnology, 2017; 16(2): 259–264

[23] Ataur Rahman M, Lee B C, Phan D T, and Chung G S. Fabrication and characterization of highly efficient flexible energy harvesters using PVDF-graphene nanocomposites. Smart Materials and Structures, 2013; 22(8):

[24] Abolhasani MM, Shirvanimoghaddam K, and Naebe M. PVDF/graphene composite nanofibers with enhanced piezoelectric performance for development of robust nanogenerators. Composites Science and Technology, 2017; 138: 49–56

[25] Marcano D C, Kosynkin D V, Berlin J M, Sinitskii A, Sun Z, Slesarev A, Alemany L B, Lu W, and Tour J M. Improved synthesis of graphene oxide. ACS Nano, 2010; 4(8): 4806–4814

[26] Hemmati S, Harris M T, and Barkey D P. Polyol Silver Nanowire Synthesis and the Outlook for a Green Process. Journal of Nanomaterials, 2020; 2020: 6–10

[27] Sağlam G, Borazan I, Hoşgün H L, Demir A, and Bedeloğlu A Ç. Effect of molar ratio of PVP/AgNO3 and molecular weight of PVP on the synthesis of silver nanowires. Nonlinear Optics Quantum Optics, 2017; 48(2): 123–132

[28] McPeak K M, Le T P, Britton N G, Nickolov Z S, Elabd Y A, and Baxter J B. Chemical bath deposition of ZnO nanowires at near-neutral pH conditions without hexamethylenetetramine (HMTA): Understanding the role of HMTA in ZnO nanowire growth. Langmuir, 2011; 27(7): 3672–3677

[29] Li M, Huang X, Wu C, Xu H, Jiang P, and Tanaka T. Fabrication of two-dimensional hybrid sheets by decorating insulating PANI on reduced graphene oxide for polymer nanocomposites with low dielectric loss and high dielectric constant. Journal of Materials Chemistry, 2012; 22(44): 23477–23484

[30] Ünsal Ö F, Altın Y, and Çelik Bedeloğlu A. Poly(vinylidene fluoride) nanofiber-based piezoelectric nanogenerators using reduced graphene oxide/polyaniline. Journal of Applied Polymer Science, 2020; 137(13): 1–14

[31] Choi S, Cho S, Yun Y, Jang S, Choi J H, Ra Y, La M, Park S J, and Choi D. Development of a High-Performance Handheld Triboelectric Nanogenerator with a Lightweight Power Transmission Unit. Advanced Materials Technologies, 2020, 5(4): 1–8

[32] Shi R, Yang P, Wang J, Zhang A, Zhu Y, Cao Y, and Ma Q. Growth of flower-like ZnO via surfactant-free hydrothermal synthesis on ITO substrate at low temperature. Cryst Eng Comm, 2012, 14(18): 5996–6003

[33] Gu L, Liu J, Cui N, Xu Q, Du T, Zhang L, Wang Z, Long C, and Qin Y. Enhancing the current density of a piezoelectric nanogenerator using a three-dimensional intercalation electrode. Nature Communications, 2020, 11(1): 1–9