Fabrication of PAN/ZnO Nanofibers by Electrospinning as Piezoelectric Nanogenerator

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Abstract. Piezoelectric nanogenerator is a material that is used for converting mechanical energy to electrical energy. This research aimed to study the piezoelectric nanogenerator properties in PAN/ZnO nanofibers layered on the stainless-steel substrate. ZnO nanoparticles that were used in this work were synthesized by coprecipitation method. The ZnO nanoparticles were mixed with PAN dissolved with DMF. Fabrication of PAN-ZnO nanofibers was done using the electrospinning method on the stainless-steel substrate. The formed PAN/ZnO nanofibers were then characterized using XRD, SEM, and FTIR. To test the piezoelectric nanogenerator properties, PAN/ZnO nanofibers were combined to PAN nanofibers and coated on the stainless-steel substrate to form piezoelectric nanogenerator device. This device was then connected to an electrometer and an oscilloscope to measure the current and voltage resulted after bending. The results of XRD of ZnO nanoparticles had the wurtzite crystal structure with the size of about 46 nm. Meanwhile, the PAN/ZnO had an amorphous structure. The test results of piezoelectric nanogenerator properties showed the value of voltage and current of 7.22 V and 47.48 μA, respectively. PAN/ZnO nanofibers on the stainless-steel substrate are potential to be the material of piezoelectric nanogenerators in general.

Keywords: PAN/ZnO nanofiber, electrospinning, piezoelectric nanogenerator, energy harvesting

1. Introduction

Nowadays, the availability of fossil energy in nature decreases due to the continual exploration to fulfill the needs of energy in the world. This is because the use of renewable energy from such sources as mechanical vibration, noise source, thermal energy, wave motion, earth heat, wind energy, and diesel fuel remains to be developed [1]. Mechanical energy becomes one of the renewable energies which can be converted into electrical energy using the piezoelectric material. This case is because the source of mechanical energy is broadly available in nature and now there is no one who utilizes it optimally. In some recent years, the development of piezoelectric-based nanogenerators (PENGs) has caught the researchers’ attention since they are potential to be a self-powered device to fulfill the energy needs in the electronic portable that still continually develops [1–3].
PENGs are usually fabricated from piezoelectric materials that have a non-centrosymmetric crystal structure such as ZnO, PZT, and BaTiO$_3$ [4]. Zinc oxide (ZnO) is one of the materials that the researchers are interested in since it has good piezoelectric, pyroelectric, and optical properties [5]. Besides, ZnO also has a relatively wide band gap of 3.37 eV [6], is non-toxic [7], relatively low cost, easily accessible [8], stable, and environmentally friendly [9]. ZnO-based PENGs generally have the output with low power [10,11] and it is less stable [12]. One of the efforts to increase the power and stability of PENGs is by using one-dimensional (1D) piezoelectric nanostructures such as nanowire, nanorods, and nanofibers [9,13,14]. PENGs in the form of nanofiber have various advantages such as having a good piezoelectric characteristic, high flexibility and it can be coated on a flexible substrate [3,7]. Besides, nanofibers can absorb mechanical energy better compared to spherical nanogenerator as nanofibers can continually distribute the mechanical force from one fiber to another fiber continually in a long time [3]. Selecting the appropriate polymer is one of the keys to form nanofibers successfully. The polymer that is commonly used is polyvinyl acetate (PVA) but the output of voltage and power resulted by ZnO/PVA nanofibers is still relatively small [3,15]. This research studied the nanogenerator properties of ZnO nanofibers by using PAN (Polyacrylonitrile) as the composite polymer for PAN molecule has a very polarized functional group [16] so that it is expected to improve the performance of PENGs in PAN/ZnO nanofibers.

2. Materials and Methods

2.1. Synthesis of ZnO nanoparticles
Fabrication of PAN/ZnO nanofibers were conducted in two steps. The first stage was a synthesis of ZnO nanoparticles using the coprecipitation method. 10 gram of zinc acetate dihydrate was dissolved into 50 ml DI water using a magnetic stirrer with the velocity of 600 rpm at the room temperature (27 °C) for 60 minutes. After that, 25 ml of NaOH 3M was dropped to Zinc acetate solution so that milky suspension was formed with pH about 13 at 90 °C, then it was let until precipitating. The deposit was then washed until the pH was neutral. Subsequently, the obtained deposit was heated at the temperature of 100 °C for 60 minutes. The formed ZnO nanoparticles were ready to be utilized in the next process.

Synthesis of PAN/ZnO Nanofibers

The second step was synthesis of PAN/ZnO nanofiber by electrospinning method. PAN/ZnO solution was prepared by weighing 0.28 g of PAN (Polyacrylonitrile) dissolved in 3.72 g of DMF and then stirred at the temperature of 80 °C with the velocity of 1000 rpm for 60 minutes. After that, 0.056 ZnO nanoparticles of the synthesis results were mixed to PAN/DMF solution and stirred for 60 minutes at the temperature of 70 °C and the velocity of 1000 rpm. This solution was then used as a PAN/ZnO nanofiber material. One milliliter PAN/ZnO composite solution was infused to 10-millimeter syringe pump. The 24G-sized syringe needle was set to the syringe and connected to the positive terminal horizontally so that the positive terminal tip (needle) and aluminum collector plate (negative terminal) had the space of 8 cm. The stainless-steel substrate (SS) was set to the collector plate that had been covered with foil aluminum. The applied debit was 10 μL/minute with the voltage of 14 kV. The formed fiber was in the form of PAN/ZnO composite fiber coated on the stainless-steel substrate. Similarly, the synthesis of PAN nanofibers was also carried out on the stainless-steel substrate (SS).

2.2. Characterization
The sample of PAN/ZnO nanofiber composite was characterized using FTIR and XRD by sloughing the composite off from the stainless-steel substrate firstly. FTIR was employed to determine the functional groups of PAN/ZnO composite. The crystal structure of ZnO nanoparticles powder and PAN/ZnO fibers were tested through XRD (X-Ray Diffraction). In the test, the nanogenerator performance was undertaken by combining two stainless steel substrates facing each other so that it formed one device. On the stainless-steel substrate, the wire was set connected to the oscilloscope and electrometer to measure the voltage and current produced from this device.
3. Results and Discussion

The diffraction pattern of ZnO nanoparticles was characterized using XRD and then analyzed using Rietica software shown in Figure 1a. The XRD pattern ZnO nanoparticles showed the hexagonal crystal structure (wurtzite) with the space group of P63mc which is in accordance with the JCPDS standard (No. 36-1451). The XRD of ZnO nanoparticles was then analyzed by refinement using Rietica software to determine the value of lattice parameter and grain size. The refinement resulted in lattice parameter of ZnO nanoparticles having \(a, b = 3.2522 \text{ Å}, \ c = 5.2095 \text{ Å}\), with the comparison of \(c/a = 1.6\) and the grain size of 46 nm. The lattice parameter which was obtained was in accordance with the lattice parameter of ZnO that previously has been reported [14,17]. In figure 1b displays the XRD pattern of PAN/ZnO nanofibers. In the diffraction pattern, it can be seen that PAN/ZnO nanofiber had an amorphous structure from PAN polymer. The XRD pattern of ZnO nanoparticles cannot be seen since their concentrations were smaller than that of PAN polymer.

Figure 1. X-Ray Diffraction Pattern of (a) ZnO nanoparticles and (b) PAN/ZnO nanofibers

Figure 2 shows the morphology of PAN/ZnO nanofibers gained from SEM-EDX results with the 20,000 times magnification. In the picture, this SEM shows that PAN/ZnO nanofibers had been formed with the diameter between 0.5 and 1 micrometer. Besides, there was an agglomeration of ZnO nanoparticles in some parts of PAN/ZnO nanofibers. From EDX test results, the synthesized PAN/ZnO nanofibers contained about 3.67% atom of ZnO elements.

Subsequently, the FTIR test was carried out to analyze the resulted PAN/ZnO nanofiber functional groups. The spectrum pattern of PAN/ZnO nanofibers is shown in Figure 3. From the result of the FTIR spectrum, it can be seen that Zn – O stretching band appeared at the wavelength of 451. This case is in line with the research conducted by Zamiri et al. (2014) reporting that the strong absorption band of ZnO was in the range of 400 to 500 cm\(^{-1}\) [18]. Besides, there was a vibration pattern at the wavelength of 3643.5, 2939.5, 2243.2, 1666.4, 1452.3, 972.1, and 451. This result was in line with FTIR pattern reported by Yar et al. (2017) for PAN nanofibers, where the vibration appeared at the wavelength of about 2934, 1414, and 1093 cm\(^{-1}\) that were the vibration of CH, CH\(_2\), and CH functional groups.
Meanwhile, the vibrations at 2241 cm\(^{-1}\) and 1662 cm\(^{-1}\) were CN and CO stretching in acrylamide [19]. FTIR pattern showed that PAN/ZnO nanofibers had been formed.

![Photo of PAN/ZnO nanofibers SEM with 20,000 times magnification](image)

**Figure 2.** Photo of PAN/ZnO nanofibers SEM with 20,000 times magnification

![FTIR Spectrum pattern of PAN/ZnO nanofibers](image)

**Figure 3.** FTIR Spectrum pattern of PAN/ZnO nanofibers

Testing the piezoelectric nanogenerator properties was performed by measuring the current and voltage using electrometer and oscilloscope. This measuring was carried out by bending in the device consisting of two stainless steel substrates coated by composite of PAN/ZnO nanofibers and PAN nanofibers facing each other. Figure 4 shows current and voltage as the time function when the device was bent and released. The average current and voltage resulted from the test were 47.48 \(\mu\)A and 7.22 V, respectively. The resulted voltage was positive and negative indicating the resulted voltage was AC voltage obtained from this research which was bigger than that attained from ZnO/PVA reported in the previous research [3].
4. Conclusion
ZnO nanoparticles that were used in PAN/ZnO nanofibers had hexagonal crystal structure (wurtzite) with the lattice parameter of $a, b = 3.2522$ Å, $c = 5.2095$ Å, with the comparison of $c/a = 1.6$ and grain size of 46 nm. Meanwhile, PAN/ZnO nanofibers obtained have the diameter size between 0.5 to 1 micrometer. The test results of piezoelectric nanogenerators properties showed the values of voltage and current were 7.22 V and 47.48 µA, respectively. These results indicated that PAN/ZnO nanofibers in the stainless-steel substrate are potential to be piezoelectric nanogenerators material.

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