The enhanced performance of piezoelectric nanogenerator by increasing zinc precursor concentration during the growth of ZnO nanorods on stainless steel foil

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Abstract. This study aims to investigate the structural and morphology of ZnO nanorods in the variation of precursor ratio on stainless steel substrate and its piezoelectric nanogenerator performance. ZnO nanorods are grown on a stainless steel substrate that has been coated with ZnO as a seed layer by a modified hydrothermal method in the variation of molar ratio between Zinc nitrate tetrahydrate (ZNT) and hexamethylenetetramine (HMT). X-ray diffraction (XRD) and scanning electron microscope (SEM) were performed for structural properties and morphology characterization. The performance of the piezoelectric nanogenerator was carried out by measuring voltage and current in applying an external force to the device. The ZnO-nanorods has a hexagonal wurtzite structure. The average length of ZnO-nanorods increased and the average diameter decreased by increasing ZNT/HMT ratio. The current and voltage of the piezoelectric nanogenerator increased with increasing by increasing the zinc nitrate ratio. These results indicate that the ZNT and HMT precursor ratio is playing an important role in the growth of ZnO nanorods that implicates the performance of the piezoelectric nanogenerator with stainless steel substrate.

Keywords: Hydrothermal method, piezoelectric nanogenerator, ZnO nanorods

1. Introduction

Fossil fuels are a major supplier of the world's energy needs at present. However, energy needs that always increase each year cause fossil fuels to be explored excessively so that their reserves in nature are depleting [1,2]. In this case, people have to look for alternatives in the use and utilization of renewable energy sources. There are several abundant energy sources can be harvested from the environment such as thermal gradient [3,4], solar energy [5,6], wind energy [7] and mechanical energy [8,9].

Energy harvesting technology based on wasted and abundant mechanical energy is very promising to be developed in self-powering and as a renewable energy application [10]. Among several types of devices that can produce energy, nanogenerator offers a promising solution because of its potential as a renewable power generation device that regenerates from pressure and vibration energy sources [11]. The piezoelectric nanogenerator is a unique technology because it can produce electricity due to the
polarization process of the charge when mechanical energy is given. The use of certain materials for the piezoelectric nanogenerator is important for alternative energy with the harvesting method.

ZnO nanorods is one of the most suitable one-dimensional semiconductors applied for piezoelectric nanogenerator [12]. ZnO has a bandgap width of around 3.37 eV and exciton binding energy of around 60 meV at room temperature [9]. ZnO nanorods can be synthesized by a simple process, relatively low temperature, low cost, and environmentally friendly through the hydrothermal method [13]. Based on these reasons, this study aims to investigate the precursor ratio between ZNT and HMT to the growth of ZnO nanorods and its piezoelectric nanogenerator performance based on the measurement of the current and the voltage in applying an external force to the device.

2. Experimental Methods
2.1 Synthesis of ZnO nanorods
Firstly, the stainless steel substrate was cleaned by an ultrasonic bath in acetone and then washed by DI water for several times. Second is the preparation of ZnO seed film by dissolving Zn-acetate dihydrate in the ethanol and then heated at 70 °C for 45 minutes. Hereafter, The Zn-acetate was mixed with MEA in equal concentration then stirred for two hours at a temperature of 70 °C and cooled in air. The spin coating technique was used for the x ZnO seed layer fabrication with at speed of 300 rpm for 25 seconds using prepared ZnO solution on stainless-steel substrate. The ZnO seed layer was annealed for two hours at a temperature of 550 °C.

Furthermore, ZnO NRs were grown using the modified hydrothermal method. The ZNT and HMT were used for the ZnO growth solution in DI water. The ZNT concentration was varied at 40 mM, 60 mM, and 70 mM, while the HMT concentration was fixed at 40 mM, yielding a molar ratio of 1:1, 1.5:1 and 1.75:1. The ZnO film was immersed at a temperature of 90 °C for six hours in the prepared solution. Then, the DI water was used for washing ZnO nanorods and dried with blower. The samples were annealed in the furnace for two hours at a temperature of 550 °C.

2.2 Characterization
The PANalytical X-ray diffraction (XRD) X’pert pro type and scanning electron microscope (SEM) FEI type Inspect-S50 were conducted to characterize the structure and morphology of the ZnO nanorods. The piezoelectric nanogenerator performance was carried out by measuring the current and voltage using an electrometer and oscilloscope in applying an external force to the nanogenerator device.

3. Results and Discussion

![Figure 1. X-ray diffraction patterns of ZnO nanorods at different ZNT/HMT ratio](image-url)
The refinement of the XRD results of ZnO NRs in three different molar ratios (1:1, 1.5:1 and 1.75:1) samples are analyzed using Rietica software as depicted in Fig. 1. All the peaks match with the Bragg peaks of ZnO and stainless steel, and no impurity phases are found in these three samples. The XRD results show the (100), (002), and (101) Bragg plane peaks at 31.08, 34.56, and 35.54, respectively. This result exhibited ZnO nanorods have been formed with the growth direction mixed between the c-axis and other direction [14]. The ZnO NRs lattice parameters are $a, b = 3.2489 (6) \, \text{Å}$, and $c = 5.2054(4) \, \text{Å}$ as accordance with the JPCDS standard (No. 36-1451). The ZnO nanorods have hexagonal wurtzite structure indicated by the ratio $c/a$ is 1.6 [15–17]. All the XRD patterns are similar for all samples that indicate there are no structural changes in the sample at different precursor ratios between ZNT and HMT.

Figure 2. SEM image and diameter distribution of ZnO nanorods at different ZNT/HMT ratio of (a) 1:1 (b) 1.5:1 and (c) 1.75:1. The insets are a cross-section of ZnO nanorods samples.

Figure 2 shows the morphology of ZnO NRs in the three different molar ratio samples possess hexagonal structure as in agreement with the results of XRD measurements. However, it appears that the length and lateral sizes of the nanorods are less homogeneous. The average lateral sizes of ZnO NRs decreases with increasing of molar ratio exhibited of 91.66 nm (1:1), 87.16 nm, (1.5:1) and 73.19 nm (1.75:1). Whereas, the average length of ZnO NRs rises with increasing molar ratio; 563 nm (1:1), 616.1 nm

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(1.5:1) and 706.9 nm (1.75:1), respectively. The concentration of precursor affects the growth of the nanorods by providing the Zn\(^{2+}\) from the zinc nitrate [18]. On the other hand, HMT serves as a weak base that slowly will be hydrolyzed in water and produces OH\(^-\) in a short time [19]. This will be very important for the nanorods growth parameter.

![Figure 3](image)

**Figure 3.** Current and Voltage as function of times at different ZNT/HMT ratio a, b) 1:1 (c,d) 1.5:1 and (e,f) 1.75:1

Figure 3 shows the results of current and voltage measurements generated from the piezoelectric properties of ZnO NRs. The ZnO NRs based piezoelectric nanogenerator device shows a peak value of current and voltage induced by external pressure. When external force works perpendicularly to the surface of ZnO NRs, piezoelectric potential then is generated along the nanorods due to the relative displacement of cations to the anion [7]. We found that the average current and voltage increases with increasing of molar ratio; 4.4 µA and 3.8 V (1:1), 8.9 µA and 11.9 V (1.5:1), 9.7 µA and 14.7 V (1.75:1),
respectively. This result indicates that the best nanogenerator performance obtained from ZnO NRs with small diameter and longest rod due to the large surface area. The output power is 142 mW/cm$^3$ which is higher compared to previously reported [20,21].

4. Conclusion
ZnO NRs were successfully synthesized using the hydrothermal method. Based on the XRD results, the ZnO NRs crystal structure is hexagonal wurtzite in agreement with SEM results exhibits the morphology of ZnO NRs is hexagonal form. The length and diameter of ZnO nanorods are 563 nm to 706.9 nm and 91.66 to 73.19 nm with increasing the precursor ratio from 1:1 to 1.75:1, respectively. The piezoelectric nanogenerator performance shows that the currents and voltages rise with increasing of increasing the Zn acetate precursor ratio. The best performance of the ZnO nanorods piezoelectric nanogenerator is 142 mW/cm$^3$ that obtained from precursor ratio between ZNT and HMT of 1.75:1.

5. References
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