Enhancing Output Voltage of Piezoelectric-Based Nanogenerators Using Zinc Oxide Material Codoped with Aluminum and Cobalt.

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Abstract. The cobalt and aluminum codoped into zinc oxide (ZnO) crystals are studied for enhancing the output voltage of piezoelectric-based nanogenerators (PENGs). The nanogenerators were simply fabricated from ZnO nanofibers (NFs) synthesized by electrospinning machine. The electrospinning processes were conducted at a flow rate of 4 µL/min and at various sintering temperature of 450, 500, 550, and 600°C. The results show that the highest output voltage of PENGs was obtained at a sintering temperature of 500°C, i.e. 127 mV. Therefore, PENGs fabricated from ZnO NFs codoped with aluminum and cobalt are challenging for the next generation of self-powered devices. The output voltage of PENGs at sintering temperatures of 450°C, 550°C, and 600°C are 75 mV, 105 mV, and 85 mV, respectively. The PENGs which fabricated from ZnO NFs was codoped with aluminum and cobalt will generate high output voltage, and are interesting candidates for exploiting in self-power devices.

Keywords: Fibers; Cobalt; Aluminum, Codoping; Zinc oxide; Electrospinning; Piezoelectric; Nano generator

1. Introduction
Piezoelectric-based nanogenerators (PENGs) are promising self-powered devices which convert mechanical energy into electrical energy [1-3]. The PENGs were commonly fabricated from piezoelectric materials having a non-centrosymmetric crystalline property; e.g. zinc oxide [2, 4], lead zirconate titanate (PZT) [5], bismuth sodium titanate (Bi₁₂Na₁₂)TiO₂₆(BNT)–barium zirconate titanate Ba(Ti,Zr)O₃ (BZT) [6], polyvinylidene fluoride (PVDF), and so forth. The materials with a non-centrosymmetric crystal are polarized between atoms and excited charge carried when subjected to an external force [7]. Among them, ZnO is a good material exploiting for PENGs because of biocompatible, biodegradable, and biosafe [8]. However, utilizing ZnO materials for PENGs are proving to have low output power density.

Many efforts have been done to enhance the performance of PENGs with ZnO materials, mainly on physical morphology [9], electrical-mechanical properties [10], and heterojunction or hybrid structures [11]. The issues in physical morphology are to vertically well-aligned ZnO nanorods with a high aspect ratio [9] and to synthesizing highly porous membrane [12]. Enhancing the electro-mechanical properties of ZnO material is commonly used by doping. Li-doped ZnO confirms that the NWs were p-type with a high carrier mobility of 14.59 cm²/V s and an effective hole carrier concentration of 1.13×10¹⁷ cm⁻³ [10].
For self-charging devices, the critical factor of PENGs is in the output voltage. PENGs with low output voltage mean that they cannot charge electrically. Therefore, enhancing the output voltage of PENGs has become essential. This study will present the sintering temperature effect for enhancing the output voltage of PENGs with ZnO NFs (nanofibers).

2. Methods
The materials which used in this study were zinc acetate dehydrate \((\text{CHOCOO})_2\text{Zn}.2\text{H}_2\text{O}\), ZnAc, Merck), aluminum chloride hexahydrate \((\text{AlCl}_3.6\text{H}_2\text{O}, \text{AlCl}, \text{Merck})\), cobalt acetate tetra hydrate \(\text{(CoCH}_3\text{COO}).4\text{H}_2\text{O}, \text{CoAc}, \text{Sigma Aldrich}\) Polyvinyl alcohol \(\text{((-C}_2\text{H}_2\text{O})_n, \text{PVA, MW 72,000, Merck})\), and aquades \((\text{H}_2\text{O})\) which used without further purification.

The fabricating of PENGs from ZnO NFs codoped with cobalt and aluminum consisted of three steps, namely (1) preparing precursor solutions, (2) producing green fibers with electrospinning machine, (3) sintering fibers, and (4) fabricating and testing PENGs. The synthesized NFs were then fabricated into PENGs and undergone for properties and performance test. The process of fabricating PENGs can be seen in Figure 1.

To prepare PVA solution, the solid PVA was mixed with \(\text{H}_2\text{O} (1:10 \text{ wt})\), stirred at 70°C for 4 hours, and followed by keeping it at room temperature for 8 hours. Subsequently, preparing the ZnAc solution was conducted by mixing 2 g ZnAc with 8 mL of water and stirring it for 1 hour at the temperature of 70°C.

ZnAc solution doped with 10 wt% of aluminum \((\text{ZnAc/Al solution})\) was prepared by mixing 4 g of ZnAc solution with 10 wt% AlCl\(_3\), then poured it into 16 ml H\(_2\)O, and stirred at a temperature of 70°C for 1 hour. The same procedure was done when preparing ZnAc solution doped with 9 wt% of cobalt to obtain ZnAc/Co solution.

The Production of ZnAc/Al/PVA and ZnAc/Co/PVA solutions were done by mixing ZnAc/Al and ZnAc/Co solution with PVA solution at a mass ratio of 1:4 and stirred for 1 hour at a temperature of 70°C.

Furthermore, preparing a ZnAc solution codoped with Al and Co at a ratio of 25% Al and 75% Co to become ZnAc/Al/Co solution was conducted by mixing ZnAc/Al/PVA solution and ZnAc/Co/PVA solution at a ratio of 25%:75%, and so forth.

Second step was producing green fibers using electrospinning process. Each precursor solution of 1 ml was injected by syringe pump at a flow rate of 4 μl / minute where the distance between electrode is 8 cm. When the high voltage was turned on, the precursor solution started to be pushed out, attracted by the electrostatic field, and attached itself on the surface of the collector plate becoming green fibers.

Step of sintering process was conducted by heating green fibers in an electric furnace at temperatures of 450, 500, 550, and 600°C for 4 hours. The purpose of sintering is to remove organic matters and to grow ZnO crystallization. The ZnO NFs were then simply fabricated into PENGs.
The output voltage of PENGs was examined by applying cyclic load of 0.5 kg in every 3 seconds. The voltage was recorded by ADAM Advantech 4018 series of data acquisition. The magnitude load of 0.5 kg was performed to represent the applied conditions of weak finger pressure [2, 13]. The performance of PENGs was then calculated based on the amount of power (Watt) generated by providing various resistances (Ohm).

3. Results and Discussion
PENGs were simply fabricated from ZnO NFs doped with Al/Co. At sintering temperatures of 450 and 500°C, the output voltage increases with the increase of the electrical resistance used. At a sintering temperature of 550°C, a large output voltage was generated at a resistance of 1 MΩ and then decreased as the resistance went up. This was more pronounce in PENGs with a small ratio of Al/Co in which Co core was easier to make in the crystallization process lead to the formation of small crystalline sizes. The resulting voltage of PENGs fabricated at a sintering temperature of 500°C can reach 127 mV and greater than those which made by the sintering temperatures of 450°C, 550°C, and 600°C, i.e. 75 mV, 105 mV, and 85 mV, respectively as shown in Figure 2.

![Figure 2](image_url)

**Figure 2.** The output voltage of PENGs fabricated with ZnO NFs doped with Al/Co at sintering temperatures (a) 450°C, (b) 500°C, (c) 550°C, and (d) 600°C.
The output voltage was also low at low electrical resistance. The high output voltage was generated at a resistance load higher than 4 MΩ. At high electrical resistance, the current is difficult to flow causing the increase of output voltage. Meanwhile, the effect of the mass ratio of codoping between aluminum and cobalt on the output voltage of PENGs did not show a regular pattern. This is due to irregularity of the orientation from ZnO NFs as seen in Figure 3. Figure 3 also showed that micro changes in diameter occur as the sintering temperature increases. The ZnO NFs have a large fiber size at a sintering temperature of 550°C compared to other sintering temperatures. The increasing sintering temperature make it more clear to see the form of ZnO NFs. However, at sintering temperatures greater than 550°C, some fibers appear to be joined to form larger fibers. This phenomenon caused the output voltage of PENGs made from ZnO NFs synthesized at sintering temperatures greater than 550 has decreased.

![Figure 3](image_url)

**Figure 3.** SEM images of ZnO NFs codoped with Al/Co and synthesized at sintering temperature (a) 450°C, (b) 500°C, (c) 550°C, and (d) 600°C.
4. Conclusions
PENGs were successfully and simply fabricated by electrospinning method from ZnO NFs doped with aluminum and cobalt. The highest output voltage of PENGs was obtained at a sintering temperature of 500°C, i.e. 127 mV. The output voltage of PENGs at sintering temperatures of 450°C, 550°C, and 600°C are 75 mV, 105 mV, and 85 mV, respectively. The PENGs fabricated from ZnO NFs codoped with aluminum and cobalt generated high output voltage, and are interesting candidates for exploiting in self-power devices.

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