

EFFECT OF SUBSTRATE AND SPIN-COATING PARAMETERS ON STRUCTURES OF ZNO NANOROD AND PVDF FILM

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Abstract

A piezoelectric nanogenerator is an energy harvesting system that converts small-scale mechanical energy into electrical energy. Zinc oxide nanorod structures have gained wide attention as a piezoelectric material for nanogenerator applications, because ZnO has good piezoelectric properties and can be fabricated at low cost. This work studied the morphology and structures of ZnO-PVDF composite films, fabricated using spray pyrolysis, hydrothermal and spin coating techniques. ZnO nanorods were grown using two steps: (1) growing seed layers on a metal substrate using a spray pyrolysis technique and (2) growing ZnO nanorods on the seed layers using a hydrothermal technique. Two different substrates, aluminium and copper foils, were used and the varying hydrothermal growth times were 12 and 14 h. The crystalline and morphological structures of the ZnO nanorods were characterized using X-ray diffraction and Scanning electron microscopy. Then, the ZnO nanorods were coated with poly (vinylidene fluoride) or PVDF using a spin-coating method with different spin speeds of 500 and 1,000 rpm. After spin-coating, the samples were treated with either air-cooling or heating (at 100°C) for 10 minutes. The phases and substituents of PVDF were analyzed using Fourier transform infrared spectroscopy (FTIR). The polar β phase of PVDF is of interest due to its piezoelectric property. The β percentage amount, calculated from the FTIR result, was maximized at 88% with ZnO nanorods and air-cooling.

Keywords: Zinc Oxide, Nanostructure, PVDF, Thin film, Nanogenerator

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Introduction

Zinc Oxide is a unique semiconductor material that exhibit various useful properties, including being optoelectronic, photocatalytic, biocompatible and piezoelectric and can be formed in a wide variety of nanostructures with low fabrication costs (Jalali, 2015; Safaei *et al.*, 2019). The piezoelectricity of ZnO nanostructures has gained broadscale attention for potential applications in vibration energy harvesters for small devices, because ZnO exhibits good electromechanical properties and can be formed into various nanostructural shapes at low temperature with high throughput. ZnO nanorod structures deposited on flexible devices have been commonly studied and have successfully harvested energy from vibration; they are known as ZnO nanogenerators (Jalali, 2015).

However, ZnO nanorod structures may be fractured in practical applications, because they cannot withstand macroscopic scale forces. Protecting the zinc oxide nanorods with a flexible polymer has been described as a useful way to improve mechanical ductility (Moonkang *et al.*, 2017). Poly (vinylidene fluoride) or PVDF has been widely researched for its piezo, pyro and ferroelectric properties. In addition, it has been widely used in applications using sensors and actuators and wearable and implantable devices, since it has properties such as flexibility and biocompatibility and it is lightweight (Mahale *et al.*, 2017).

PVDF is a semi crystalline polymer and has at least four crystalline phases, depending on the processing conditions. Among the four crystal phases, the α phase is the most common in PVDF; however, it is non-polar (Lanceros-Mendez *et al.*, 2001). The polar β phase shows piezo, pyro, and ferroelectric characteristics due to all trans-conformation (Panda *et al.*, 2020). The γ phase is an immediate conformation of the α and β phase. The δ phase is a different packing structure of the PVDF α phase (Nishiyama *et al.*, 2001). Thus, the amount of β phase crystal should be as high as possible to enhance the piezoelectric property of PVDF, which is ideal for vibration energy harvesting applications. The enhancement of β phase content is possible by incorporation of a nanostructure in the polymer formation due to the large surface area of interaction. It has been reported that the addition of a piezoelectric material ZnO to PVDF can help increase the β phase and its piezoelectric property due to its high aspect ratio nanostructure (Panda *et al.*, 2020).

The current study investigated the effect of the ZnO nanorod substrate and spin-coating

parameters on the formation of the PVDF β phase. ZnO nanorods were grown on two different substrates (aluminium and copper foils) using a spray pyrolysis technique and subsequent hydrothermal methods. The spray pyrolysis and hydrothermal processes are low-cost techniques that can be applied on a large scale to produce ZnO nanorod structures. Then, the ZnO-PVDF composite was prepared using a spin coating method with varying spin speed and different curing treatments (air cooling and baking at 100°C for 10 minutes). The current work reports on the analysis using systematic study of the influence of substrates, hydrothermal time, spin speed and treatment after spin coating.

Materials and methods

Synthesis of ZnO nanorods

Zinc oxide nanorods were prepared using two steps: (1) ZnO seed layer deposition by a spray pyrolysis technique and (2) ZnO nanorod growth using a hydrothermal process, as shown in Figure 1. The spray-pyrolysis equipment used in the spray pyrolysis technique was designed and built in-house, as reported by Sripianem *et al.* (2018), and Sripianem and Techapiesancharoenkij (2018). The substrate was cleaned with acetone and deionized water for 10 minutes each in an ultrasonic cleaner. Aluminium (Al) and copper (Cu) foils were studied as the two types of substrates. The ZnO seeding solution was prepared with 0.05 M Zinc acetate dissolved in methanol and then magnetically stirred for 10 minutes. The prepared solution and the compressed carrier gas were fed through the nozzle and sprayed uniformly on the substrate for 10 minutes at 400°C. The flow rate was set at 4 ml. min⁻¹ and the pressure was 0.2 kg cm⁻² for the whole process of seed layer deposition (Sripianem *et al.*, 2018; Sripianem and Techapiesancharoenkij, 2018).

The hydrothermal growth of ZnO nanorod structures used 0.025 M zinc nitrate dissolved in deionized water and magnetically stirred for 30 minutes. After that, 0.025 M hexamethylenetetramine was added to deionized water and stirred for 30 minutes. Then, the two solutions were mixed with equal volumetric proportions for 15 minutes until the mixture became homogeneous. The substrate with the ZnO seed layer deposition was placed in the autoclave together with the prepared solution and heated at 90°C for either 12 h or 14 h. After autoclaving, the

sample was cleaned with deionized water and heated at 90°C for 10 minutes.

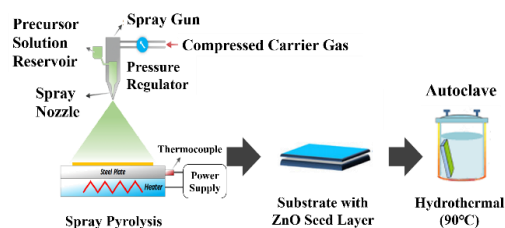


Figure 1. Fabrication of ZnO nanorods on a metal foil using spray pyrolysis technique for ZnO seed layer and hydrothermal method for ZnO nanorod growth

X-ray Diffraction (XRD) Analysis

The structural phases of the ZnO nanorod films were characterized using XRD ($\text{CuK}\alpha$ radiation X-rays of wavelength 1.54 Å, 40 kV, 30 mA), using a Philips X'Pert X-ray diffractometer. The diffraction patterns were captured for 2θ values ranging from 20° to 70° with a step size of 0.02°.

Scanning Electron Microscopy (SEM)

The surface morphology and morphological analysis of the ZnO nanorod films were analyzed using SEM (SU3500, Hitachi), after gold sputtered coating. Images were captured in a secondary electron mode at 10kV accelerating voltage and 3,500× magnification. Elemental mapping was measured using energy dispersive spectrometry (EDS).

Preparation of PVDF solution for spin coating

A PVDF solution was prepared by dissolving PVDF powder (1.5g) in 20 ml of N, N-dimethylformamide (DMF) and acetone (ratio 2:3) at room temperature. The solution was stirred for 4 h to obtain a homogeneous solution.

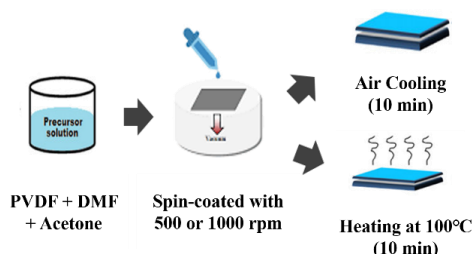


Figure 2. Schematic diagram of spin coating of PVDF on ZnO nanorod substrate

Preparation of ZnO-PVDF

The process for spin-coating of PVDF on the ZnO nanorod layer is shown in Figure 2. ZnO-PVDF films were prepared by spin coating the PVDF solution on the substrate at room temperature with varying spin speeds (500 rpm or 1,000 rpm) for 2 minutes. Then, samples were cured using two varying methods for comparison: (i) air cooling for 10 minutes and (ii) heating at 100°C for 10 minutes. The PVDF films were also spin-coated at 500 rpm or 1,000 rpm on an Al foil or a Cu foil without ZnO layer as the control samples.

Fourier transform Infrared (FTIR) spectroscopy

The molecular vibrations and the existence of substituents of PVDF films and ZnO-PVDF films were analyzed using FTIR spectroscopy of wave numbers in the range 700-1400 cm^{-1} using a Bruker Alpha-E spectrometer.

Results and discussion

Characterization of ZnO nanorods

The representative XRD spectra of the ZnO seeding layers on Al and Cu foils are shown in Figure 3. The presence of ZnO peaks with the hexagonal wurtzite structure, containing the (100), (002), and (101) peaks, was observed for the ZnO seeding layers on Al foil. However, for the ZnO seeding layers on Cu foil, the ZnO peaks were much lower relative to the Cu peaks of (111) and (200), indicating that the ZnO seeding layers formed better on the Al foil than the Cu foil under the spray pyrolysis conditions in this work.

The representative XRD spectra of the ZnO nanorods on Al foil and Cu foil are shown in Figure 4. All the peaks showed ZnO with the hexagonal wurtzite structure, containing the (100), (002), and (101) peaks, was observed for both the Al and Cu foils. All the diffraction peaks indicated the ZnO nanorods had a lattice $c=0.5206$ nm. For the ZnO nanorods on Al foil, the (002) peak had a higher intensity than the other two peaks, implying the preferential growth direction of c-axis (perpendicular to the (002) plane). For the ZnO nanorods on Cu foil, the relative intensities of the Cu diffraction peaks were much higher than for the ZnO peaks. However, the ZnO dominant peak intensity is (101) instead of (002), implying that the columnar alignment of the nanorod preferential growth of c-axis (perpendicular to (002) plane) is not fully upright, as compared to those on the Al foil. Hence, the alignment of the ZnO nanorods differed between the Al and Cu substrates.

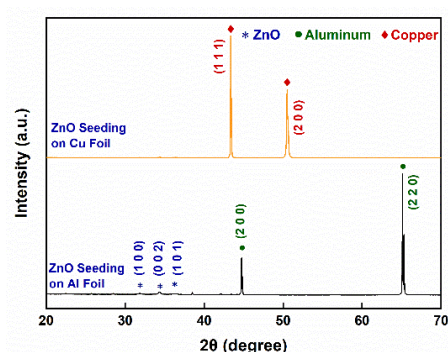


Figure 3. Representative XRD spectra of ZnO seed layers on Al and Cu foils

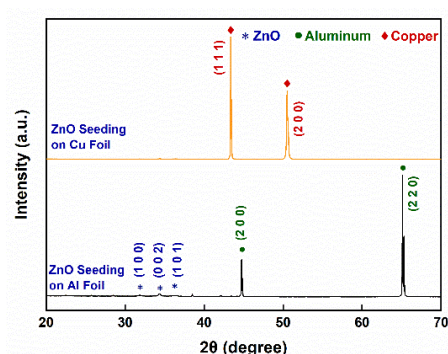


Figure 4. Representative XRD spectra of ZnO nanorods on Al and Cu foil with hydrothermal growth times of 12 and 14 h.

Table 1. Crystallite sizes of ZnO nanorods synthesized using spray pyrolysis and hydrothermal methods on Al and Cu foils with either 12 h or 14 h hydrothermal periods

Sample	Crystallite size (1 0 0)	Crystallite size (0 0 2)	Crystallite size (1 0 1)
ZnO on Al foil (12h)	32nm	58nm	35nm
ZnO on Al foil (14h)	39nm	56nm	43nm
ZnO on Cu foil (12h)	31nm	49nm	17nm
ZnO on Cu foil (14h)	32nm	48nm	18nm

Table 1 shows the calculated crystallite size of ZnO nanorods on different substrates corresponding to the X-ray diffraction planes, using Scherrer's technique. Generally, for both the Al and Cu foils, the calculated crystallite sizes of the ZnO nanorod growth using a 12-h hydrothermal time was almost the same as for using a 14-h hydrothermal time. The crystallite sizes of the ZnO nanorods on the Cu foil were smaller than those of the ZnO nanorods on the

Al foil. For the same hydrothermal solution and time in this study, the ZnO nanorods appeared to grow with a better-upright alignment and larger grains on the Al foil than on a Cu foil.

Surface Morphology of ZnO nanorods

Figure 5 shows the SEM images of the ZnO seed layers on Al and Cu foils. The ZnO seed layers on the Al foil were denser and better-formed than those on the Cu foil, which agreed with the XRD results above.

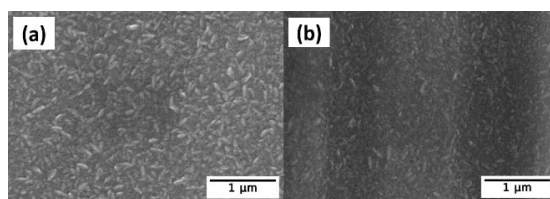


Figure 5. SEM images of ZnO seed layer on (a) Al foil and (b) Cu foil

The SEM images of the ZnO nanorods on the Al and Cu foils are shown in Figure 6. Corresponding well with the XRD analyses above, the nanorods grow thicker on Al foil than on Cu foil. The ZnO nanorods on the Al foil had an average diameter of 300 nm compared to those on the Cu foil that had an average diameter around 170 nm, as shown in Figure 6. The thick ZnO nanorods on the Al foil appeared to be aligned upright better than the thin, small ZnO nanorods on the Cu foil. The upright ZnO nanorod on the Al foil corresponds with the preferential peak of (002) for the XRD result (Figure 4), while the thin ZnO nanorods on the Cu foil are tilted with poor alignment, resulting in the preferential plane of (101) instead. The well-formed and uniformly dispersed seed layers on the Al foil provided a good foundation for the ZnO nanorods to grow on, as opposed to the layers on the Cu foil. The EDS analysis was carried out to determine the elemental composition of the ZnO nanorods. Figure 7 and Figure 8 provide the EDS examples of the ZnO nanorods on the Al and Cu foils, respectively, showing strong peaks of Zn, O, Al, and Cu without any impurity peaks. An Au peak is expected because the samples were coated with Au for the SEM analysis.

FTIR Analysis of PVDF and ZnO-PVDF

The FTIR spectra of the PVDF spin-coated on a substrate (PVDF) and the PVDF spin-coated on the ZnO nanorod/foil (ZnO-PVDF) can be seen in Figure 9 (for the Cu foil substrates) and Figure 10 (for the Al foil substrates). The peak at 760 cm^{-1} indicates the presence of the α phase attributed to

CF₂ wagging (Lanceros-Mendez *et al.*, 2001). The main peak of γ which is one of the electroactive phases was found at 1232 cm⁻¹ (Biswas *et al.*, 2017). The peak at 840 cm⁻¹ was due to CF₂ stretching and CH₂ rocking, which also show the existence of the β phase (Lanceros-Mendez *et al.*, 2001; Panda *et al.*, 2020). At wavenumber 880 cm⁻¹, there was a strong peak related to the skeleton C-C-C stretching bond; all the substituents of the PVDF structure were found in the FTIR results (Lanceros-Mendez *et al.*, 2001). It was observed that the β phase absorption peak intensity at 840 cm⁻¹ in PVDF increased with the presence of the ZnO nanorod layers as to the PVDF without the ZnO nanorod layers. At 1275 cm⁻¹, the β peak was more visible for the air-cooled samples, while the characteristic band of the β phase had almost diminished compared to the heating-cured samples. The amount of β phase can be calculated using Equation 1:

$$F(\beta) = \frac{A(\beta)}{1.26 \times A(\alpha) + A(\beta)} \quad (1)$$

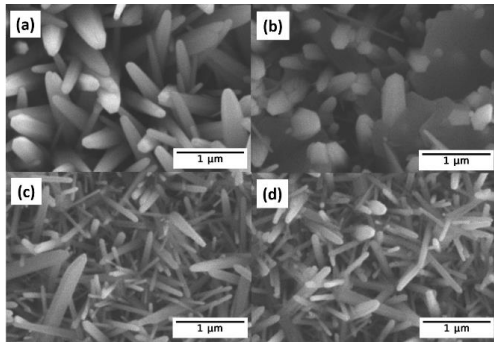


Figure 6. SEM images of ZnO nanorods on Al foil with hydrothermal growth periods of (a) 12 h and (b) 14 h and on Cu foil with hydrothermal growth period of (c) 12 h (d) 14 h.

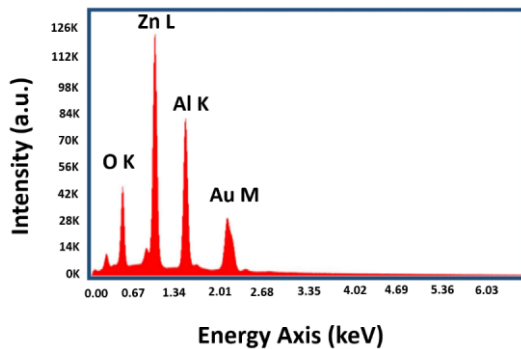


Figure 7. Representative EDS spectrum of ZnO nanorods on Al foil

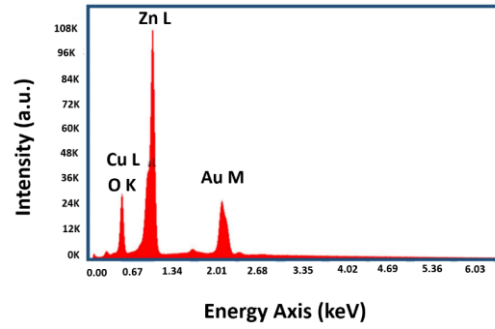


Figure 8. Representative EDX spectrum of ZnO nanorods on Cu foil

where $A(\beta)$ is the absorption intensity of β phase at 840 cm⁻¹ and $A(\alpha)$ is the intensity of α phase at 761 cm⁻¹ (Lee *et al.*, 2015).

The calculated β phase fractions for all the samples are summarized in Table 2 (for the Cu foil substrate) and in Table 3 (for the Al foil substrate). Notably, the air-cooled samples had higher β -phase fractions than the heating-cured samples because the temperature affected the crystallization rate during the curing process of PVDF. At high temperature, the crystallization rate of PVDF increases which favors α phase formation. At a temperature lower than 60°C, there is enough time for the nucleation and growth of the β phase (Mahale *et al.*, 2017). Therefore, air-cooling can be considered as a suitable treatment after PVDF spin-coating, as it can enhance the β -phase fraction.

Table 2. Calculated β phase fraction for PVDF and ZnO-PVDF on Cu foil at different spin speeds

Sample	β -Phase Fraction
PVDF (Air-500 rpm)	0.79
PVDF (Heating-500 rpm)	0.63
PVDF (Air-1,000 rpm)	0.57
PVDF (Heating-1m000 rpm)	0.55
ZnO-PVDF (Air-500 rpm)	0.88
ZnO-PVDF (Heating-500 rpm)	0.70
ZnO-PVDF (Air-1,000 rpm)	0.85
ZnO-PVDF (Heating-1,000 rpm)	0.68

Table 3. Calculated β phase fraction for PVDF and ZnO-PVDF on Al foil at different spin speeds

Sample	β -Phase Fraction
PVDF (Air-500 rpm)	0.72
PVDF (Heating-500 rpm)	0.60
PVDF (Air-1,000 rpm)	0.78
PVDF (Heating-1,000 rpm)	0.77
ZnO-PVDF (Air-500 rpm)	0.88
ZnO-PVDF (Heating-500 rpm)	0.84
ZnO-PVDF (Air-1,000 rpm)	0.83
ZnO-PVDF (Heating-1,000 rpm)	0.82

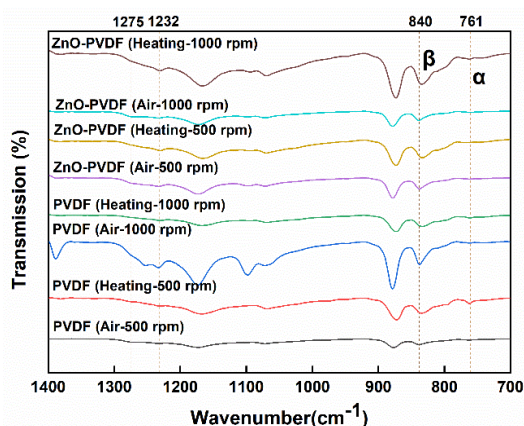


Figure 9. FTIR spectra of the PVDF on a Cu foil (PVDF) and the PVDF on ZnO nanorod/Cu foil (ZnO-PVDF) under either air-cooled or heating curing with different spin speeds of 500 or 1,000 rpm.

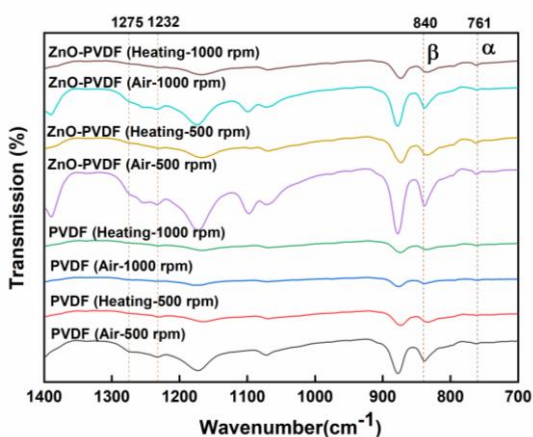


Figure 10. FTIR spectra of the PVDF on a Al foil (PVDF) and the PVDF on ZnO nanorod/Al foil (ZnO-PVDF) under either air-cooled or heating curing with different spin speeds of 500 or 1,000 rpm.

For air-cooling PVDF on the Cu foil (Table 2), with the presence of the ZnO nanorod layers, the relative β -phase fraction increased from 0.79 to 0.88 and from 0.63 to 0.70 for 500 rpm and from 0.57 to 0.85 for 1,000 rpm. For air-cooling PVDF on Al foil (Table 3), the β -phase fraction increased from 0.72 to 0.88 (500 rpm) and from 0.78 to 0.83 (1,000 rpm). The nucleation of the β phase in ZnO-PVDF involves the interaction between the CH_2 of the PVDF chains (having a positive charge density) and the ZnO nanorods (having a negative charge density) (Jingjing *et al.*, 2019). However, for the 500 rpm and 1,000 rpm samples for ZnO-PVDF, there

was not much different in the β -phase fraction values, with differences of only 0.02 or 0.03. The studied spin coating speed (500 and 1,000 rpm) appeared to have a negligible effect on β -phase formation for ZnO-PVDF. For ZnO-PVDF on either the Al or Cu foils, the β -phase fractions were comparable with the optimum values of 0.88 for both substrates.

Overall, the $F(\beta)$ value was higher in ZnO-PVDF than in PVDF. The presence of the ZnO nanorods helped increase the $F(\beta)$ value, which potentially could enhance the piezoelectric response. The β -phase fraction was higher in the air-cooling samples as opposed to the heated samples. The calculated $F(\beta)$ was highest (88%) for the ZnO-PVDF nanocomposite with air treatment. Therefore, incorporating ZnO nanorods could enhance the β crystals in the PVDF. Hence, increasing the β phase would be expected to help increase the piezoelectric response for energy harvester applications, which will be investigated in the near future.

Conclusion

Zinc oxide nanorods were successfully synthesized using spray pyrolysis and a hydrothermal method. The XRD and SEM analyses showed that the ZnO seed layers formed better on the Al foil than the Cu foil under the spray pyrolysis conditions in this work. The ZnO seed layers on the Al foil were denser and better-formed than those on the Cu foil. As a result, the ZnO nanorods on Al foil appeared to be larger and more aligned than those on Cu foil. ZnO-PVDF was fabricated using a spin coating method with different spin speeds of 500 rpm or 1,000 rpm and two different post treatments of air-cooling and heating at 100°C. The β -phase fraction value was higher in ZnO-PVDF than in PVDF. Furthermore, the β -phase fraction was higher in the air-cooled samples as opposed to the heated samples. The calculated β phase fraction was highest (88%) for the ZnO-PVDF nanocomposite with air treatment.

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