

Application of ZnO Nanoparticles EM Wave Detector Prepared by Sol-gel and Self-Combustion Techniques

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Abstract. Zinc oxide (ZnO) has found many important applications such as optoelectronic devices, sensors and varistors. The challenging part however is synthesizing ZnO nanoparticles and its utilisation as EM detectors. Sol-gel and self-combustion techniques were chosen in this study due to the ability to produce single phase and nano-size samples. The starting mixture consists of 10 grams of zinc (II) nitrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt which was dissolved in 50 mL of nitric acid, HNO_3 . The solution was stirred at 250 rpm continuously for 1 day. The mixture was then gradually heated for every 15 minutes until it combusted at 110°C for the self-combustion technique. For the sol-gel technique, the dissolved mixture was heated at 40°C , 50°C , 60°C and 70°C until the gelatine was formed. After the drying process, the as-prepared samples were annealed at 100°C and 200°C for 1 hour for each technique. Characterizations were performed by using X-Ray Diffraction (XRD), Raman Spectra and Scanning Electron Microscopy (SEM). The XRD analysis showed a major peak of [101] plane at 2θ for the self-combustion technique and the sol-gel technique. Raman results for the samples prepared via sol-gel and self-combustion techniques had shown the major peak of ZnO that is located at the Raman shifts of 437.67 cm^{-1} . Using the Scherrer equation, single crystal nano particle of ZnO was successfully obtained in the range of 38.49 nm to 50.70 nm for the sample prepared via the sol gel technique. By the self-combustion technique, the average dimension of the as-prepared sample is in the range of 34-49 nm. Further heat treatment resulted in a major change of the Raman shift corresponding to the single phase ZnO nano particles. The best samples were used as electromagnetic (EM) detectors. The EM detectors are polymer based composite which were prepared using a casting technique.

Introduction

Zinc oxide is a unique and very useful material to date. Zinc oxide has a stable wurtzite structure with a lattice spacing $a = 0.325\text{ nm}$ and $c = 0.521\text{ nm}$ [1]. Various ZnO nanostructures with different morphologies such as nanorods [2,3], nanotubes [4], nanosphere [5], nanoneedles [6] etc have been reported. These nanostructures have been fabricated with different methods such as hydrothermal [1,7,8], precipitation [9], sol-gel [5,6,10], simple thermal sublimation [11], self-combustion [12], vapour liquid solid [3,13], double jet precipitation [14], polymerized complex method [15], polyol method [16] etc. Zinc oxide nanostructure materials can be used for devices like solar cells, sensors, detectors and energy generators [7] and other transparent conducting oxides [17]. ZnO has optically excellent properties such as a wide band gap (3.37 eV) [1,4,18] and a large exciton binding energy (60 meV) at room temperature [1,4]. ZnO has electrical properties and a

band gap energy similar to TiO_2 and it has been reported sometimes to be more efficient than TiO_2 [5]. The lowest resistivity, $0.2 \Omega\text{m}$, was obtained for pure ZnO after annealing in Ar [10]. In addition, ZnO is on the borderline between a semiconductor and an ionic material [12]. The chemical reduction of crystal yields oxygen vacancies which act as donors and current voltage characterization of ZnO single crystals at 77 K [19]. This would be the basis of our intention of using ZnO particles as EM detectors. This paper reports novel synthesis techniques, sol-gel and self combustion and their physical characterization. Both the sol-gel and the self-combustion are powerful methods for tailoring transition metal oxides for detection applications [5]. The ZnO nanoparticles are used as electromagnetic (EM) detectors.

Experimental procedures

Synthesis of ZnO Nanoparticles. ZnO nanoparticles were prepared by employing two techniques, which are the sol-gel and self-combustion techniques. This process began with dissolving zinc nitrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt into 65% concentrated nitric acid, HNO_3 solution for each technique. Both solutions were stirred for 1 day to form a homogeneous sol. For sol-gel, the homogenized sol solution was then heated up at 40°C , 50°C , 60°C and 70°C until the gelatin was formed. Meanwhile, the homogenized sol solution was also heated until it combusted at 110°C for the self-combustion technique. Both samples were dried in an oven at 110°C for 24 hours. The dried samples were crushed for 1 hour to obtain fine particles. After the crushing process, the green powders were annealed at 100°C , 200°C , 300°C and 400°C [21] for 1 hour for both techniques.

Synthesis of EM detector (Polyvinyl Alcohol + as-prepared ZnO). The starting mixture consists of 3.6 g of PVA powder which was dissolved in 160 mL of deionizer water. The solution was manually stirred at 60°C until the PVA powder was dissolved. The thick solution was divided into two parts, the first part consists of pure PVA and the second part consists of PVA + ZnO (sol-gel powder, annealed at 300°C). All the samples were placed in a petri dish. Later, the samples were dried under a spotlight for about 12 hours. The dried polymers were cut into rectangular shape with the size of 6.5 cm x 2.5 cm. The average thickness of the samples is approximately 0.04 mm.

Characterization of Particles. The samples were then characterized by X-Ray Diffraction (XRD), Raman Spectra and Scanning Electron Microscopy (SEM). Characterization of zinc oxide is to obtain information about its crystallinity and morphology [12]. The energy dispersive technique was used to give the elementary analysis of the ZnO annealed powder. The electromagnetic detection set up was published elsewhere [20].

Results and discussion

X-Ray Diffractions (XRD). Figure 1 and Figure 2 show the XRD patterns of the as-prepared ZnO samples that were prepared by sol-gel and self combustion techniques, respectively. All peaks appeared are matched with a standard card, for each of the samples at annealed 100°C , 200°C , 300°C and 400°C by using both techniques (Table 1).

Table 1. Standard Card of Zinc Oxide.

Sample	Standard Card
ZnO SG(100°C)	SS-NNNN 72-0627
ZnO SG(200°C)	SS-NNNN 89-0511
ZnO SG(300°C)	SS-NNNN 65-3411
ZnO SG(400°C)	SS-NNNN 79-2205
ZnO SC(100°C)	SS-NNNN 89-1397
ZnO SC(200°C)	SS-NNNN 79-2205
ZnO SC(300°C)	SS-NNNN 89-0511
ZnO SC(400°C)	SS-NNNN 89-0510

The samples prepared by the sol-gel method show the [101] major peak at 2θ of 9.33° , 36.29° and 36.27° , 36.29° which was annealed at 100°C , 200°C , 300°C and 400°C , respectively. Meanwhile for the self-combustion method, the [101] major peak was observed at 2θ of 36.18° , 36.26° , 36.29° and 36.27° for samples that were annealed at 100°C , 200°C , 300°C and 400°C , respectively. This result is consistent with other research done [12].

By applying the Scherrer equation [12,14], which is given in Equation [1], the average crystallite size can be obtained:

$$D = \frac{0.89\lambda}{\beta \cos \vartheta} \quad (1)$$

where: λ is the X-ray wavelength, θ is the Bragg diffraction angle, β is the peak width at half-maximum.

The average crystallite size of the ZnO samples that were prepared via the sol-gel method annealed at 100°C and 200°C are 38.49 nm and 50.70 nm respectively. But when the annealing temperature increased to 300°C , there was a slight decrease in the crystal size (Table 1). For the self-combustion technique, the average crystallite size is 34.58 nm for a sample annealed at 100°C and 48.63 nm for a sample annealed at 200°C (Table 1). Referring to the Full Width Half Maximum (FWHM) values, it is obvious that all of the as-prepared samples exhibit larger values indicating smaller particle size.

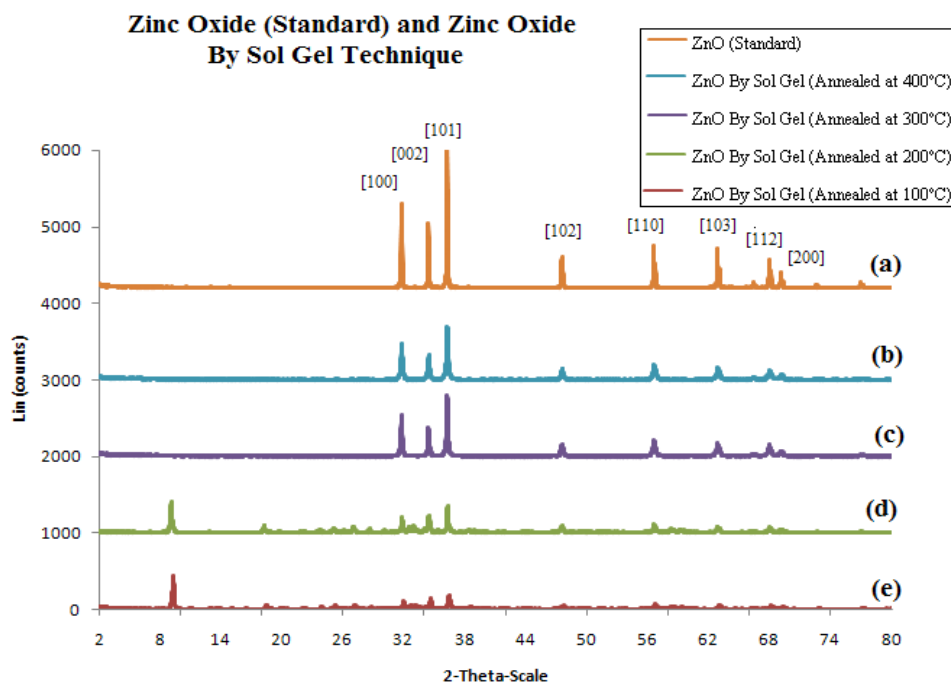


Figure 1. XRD patterns of as-synthesized zinc oxide samples with a major peak [101] (a) zinc oxide standard; and samples prepared via sol gel technique that were annealed at (b) 400°C and (c) 300°C (c) 200 °C and (d) 100°C.

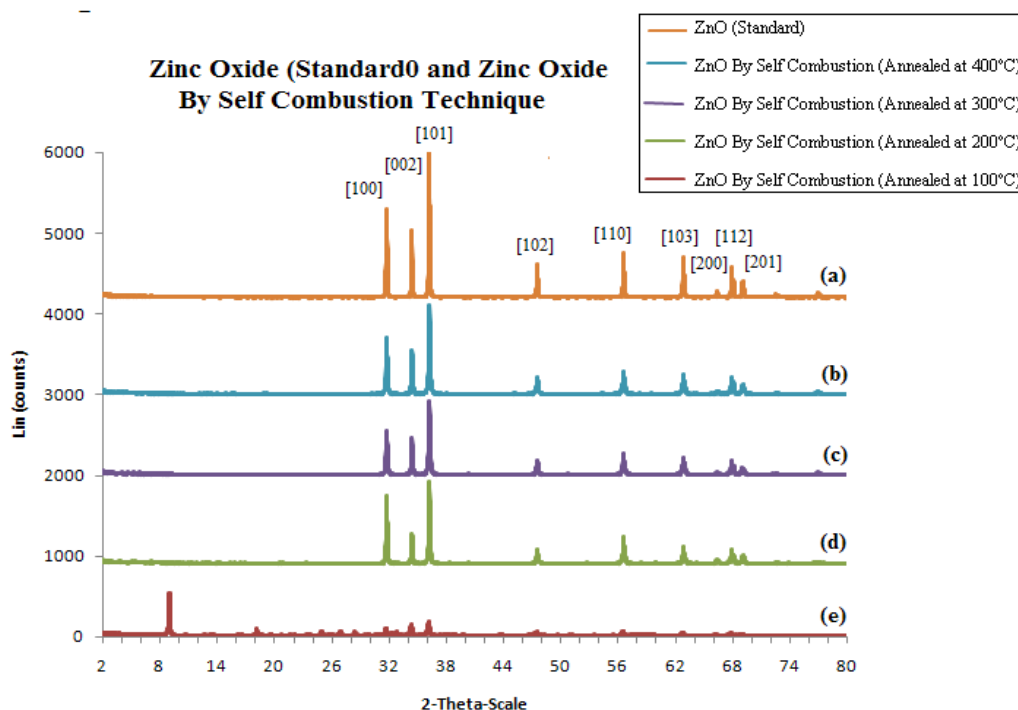


Figure 2. XRD patterns of as-synthesized zinc oxide samples with a major peak [101]; (a) zinc oxide standard; and samples prepared via the self combustion technique that were annealed at (b) 400°C and (c) 300°C (d) 200°C (e) 100°C.

Table 1. XRD and RAMAN Results.

Samples	X-Ray Diffraction							Raman Spectroscopy	
	Intensity (Counts)	FWHM	d-spacing (Å)	Crystallite size (nm)	A	b	c	Raman Shift (cm ⁻¹)	Intensity (Counts)
ZnO SG(100°C)	9.332	0.222	9.469	38.490	19.48	6.238	5.517	1055.300	42.140
ZnO SG(200°C)	36.287	0.163	2.473	50.700	3.249	3.249	5.205	1055.300	36.569
ZnO SG(300°C)	36.269	0.201	2.474	33.290	3.249	3.249	5.269	439.696	55.048
ZnO SG(400°C)	36.285	0.216	2.4737	38.290	3.250	3.250	5.207	438.177	43.830
ZnO SC(100°C)	36.178	0.239	2.480	34.580	3.253	3.253	5.213	437.670	28.438
ZnO SC(200°C)	36.264	0.170	2.475	48.630	3.250	3.250	5.207	437.670	20.186
ZnO SC(300°C)	36.269	0.186	2.474	44.450	3.249	3.249	5.205	433.115	20.087
ZnO SC(400°C)	36.271	0.175	2.474	47.240	3.248	3.248	5.205	440.203	46.515
ZnO (Standard)	36.251	0.113	2.476	n.a	3.250	3.250	5.207	437.171	31.5891

n.a: not available

Raman Spectra. Based on the Raman spectroscopy results, the intensity of the Raman shift of the zinc oxide samples decreases when the annealing temperature was increased to 200°C. For sol-gel samples, it shows that the Raman shift are 1055.3 cm⁻¹ (for samples annealed at 100°C and 200°C), 439.696 cm⁻¹ (for samples annealed at 300°C) and 438.177 cm⁻¹ (for samples annealed 400°C).

The self-combustion samples show the Raman shift at 437.67 cm⁻¹ (annealed at 100°C and 200°C), 433.11 cm⁻¹ (annealed at 300°C) and 440.203 cm⁻¹ (annealed 400°C). These two major shifts are known as second order Raman shift are in the same range of reported values which are 323- 1120 cm⁻¹ shifts [12,24]. It was found that when we further annealed the samples up to 400°C, the major Raman shift can be observed. Observing all the samples prepared by the self-combustion technique, the major Raman shift approximately at 337 cm⁻¹ can be observed indicating single phase. Both the XRD and the Raman spectra analysis indicated that sol-gel and self-combustion techniques had resulted in single ZnO phase.

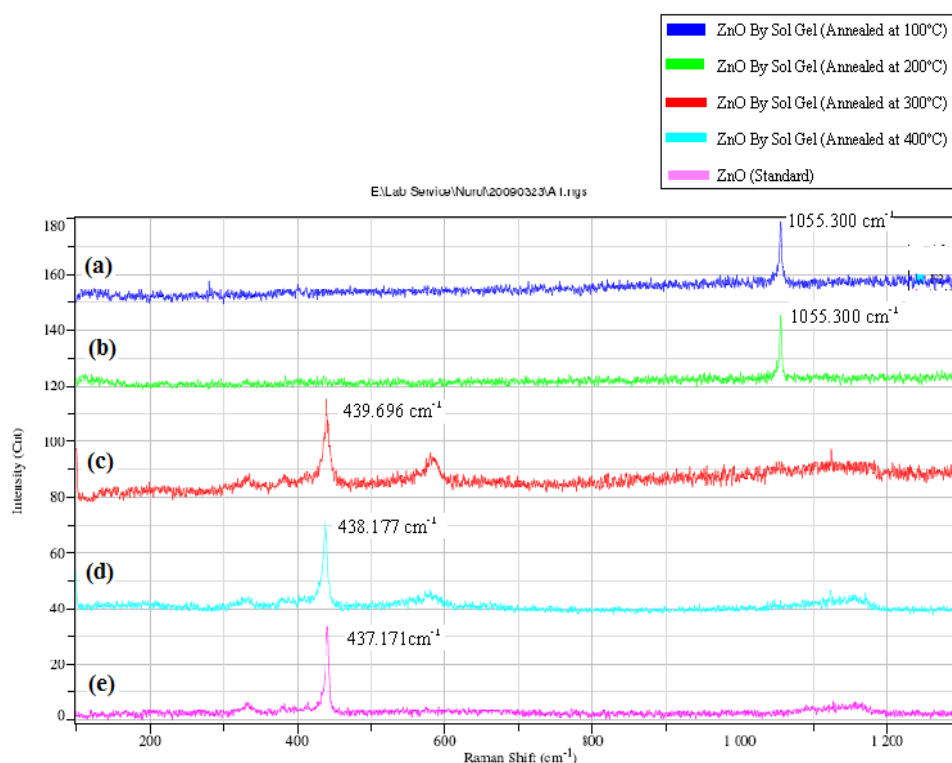


Figure 3. Raman results Sol Gel Technique with Annealing at (a) 100°C; (b) 200°C; (c) 300°C (d) 400°C and (e) Standard Zinc Oxide Raman Shift.

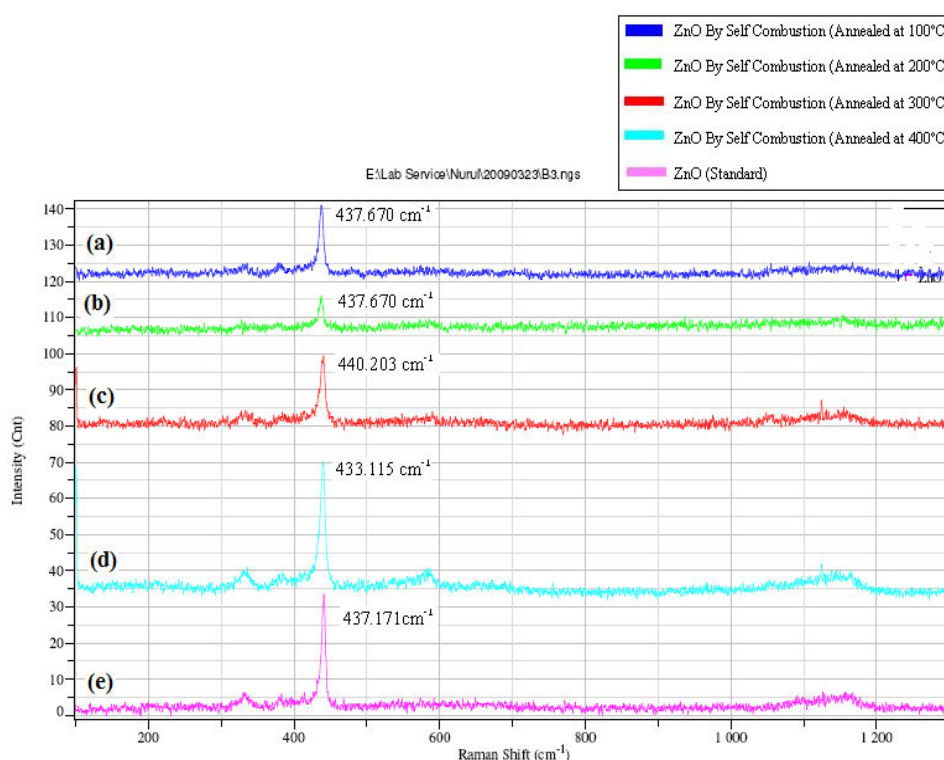


Figure 4. Raman results Self Combustion Technique with Annealing at (a) 100°C; (b) 200°C; (c) 300°C (d) 400°C and (e) Standard Zinc Oxide Raman Shift.

Scanning Electron Microscope (SEM) Results. The SEM images show that the two different synthesis methods had resulted in different morphologies despite the single phase structure. By using the sol-gel technique, ZnO flakes were observed. On the other hand, the ZnO rods morphology was observed when the samples were prepared using the self combustion technique. Generally increasing annealing temperature would result in increasing the grain size [22,23].

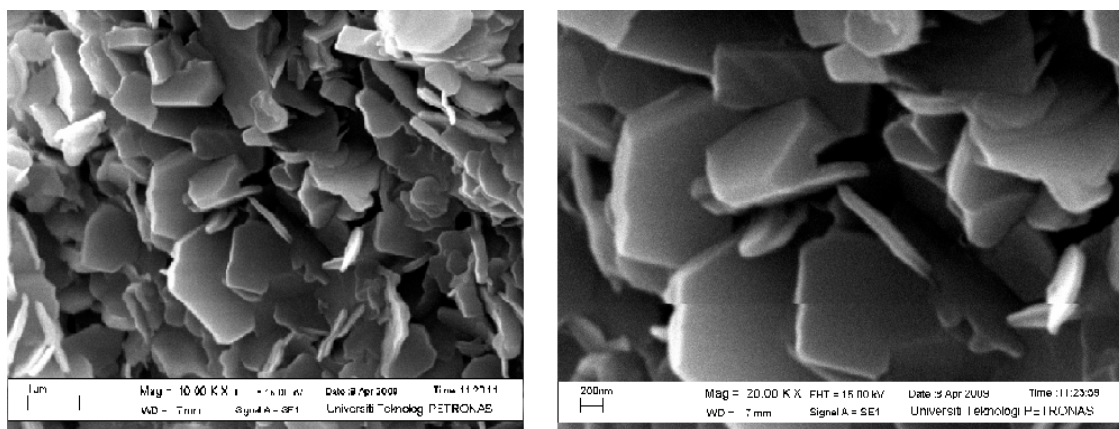


Figure 5. SEM morphology of nanorods at two different magnifications (annealing at 200°C) by using the Sol-Gel technique.

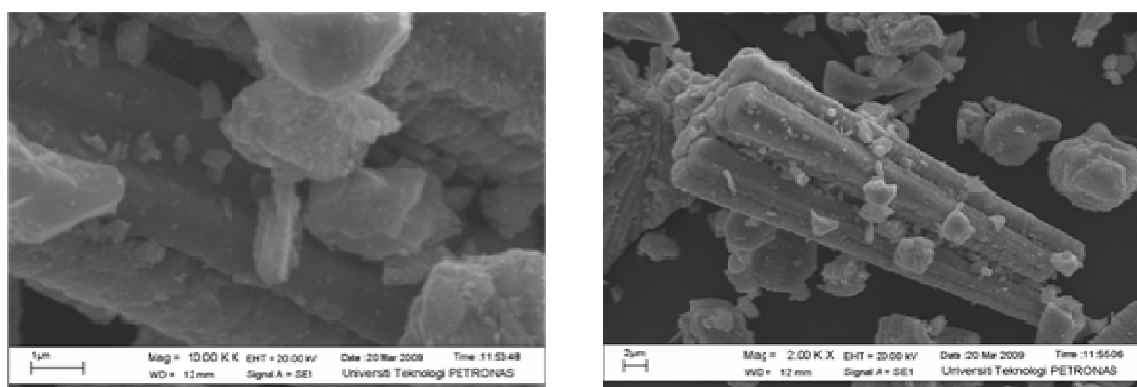


Figure 6. SEM morphology of nanorods at two different magnifications (annealing at 200°C) by using self combustion.

Energy Dispersive X-Ray (EDX) Results. This technique is used to study the elemental properties of the ZnO samples. Energy dispersive X-ray gives an elemental analysis or analysis of a sample. Referring to the periodic table, the weight of zinc is 80.34% and oxygen is 19.65%. Referring to Table 2, samples that were prepared using the sol-gel (100°C) method gives a closer weight percent and atomic percent to the theoretical value.

Table 2. EDX of Zinc Oxide Samples.

	Sol Gel at annealing 100°C		Sol Gel at annealing 200°C		Self Combustion at annealing 100°C		Self Combustion at annealing 200°C	
	Zn	O	Zn	O	Zn	O	Zn	O
Weight (%)	81.30	18.70	55.85	44.15	64.55	29.55	93.25	6.75
Weight Percentage Error (%)	1.19	4.89	30.48	124.57	19.65	50.31	16.07	65.67
Atomic (%)	51.56	48.44	23.64	76.36	29.69	55.54	77.16	22.84
Atomic Percentage Error (%)	3.12	3.12	52.72	52.72	40.62	11.08	54.32	54.32

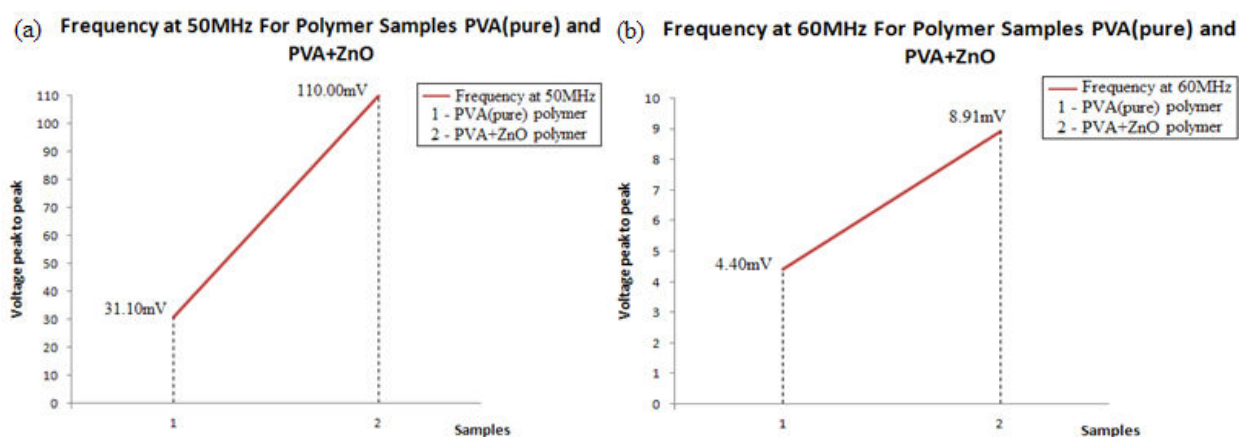


Figure 7. The voltage peak to peak (Vpp) of a detectors (a) Polymer samples PVA(pure) and PVA+ZnO is at 50 MHz; (b) Polymer samples PVA(pure) and PVA+ZnO at 60 MHz.

Observing Figure 7 it shows that PVA+ZnO polymer sample had shown the higher voltage peak to peak (Vpp) comparing to the PVA polymer without ZnO as filler. At 50 MHz, the PVA polymer sample and the PVA-ZnO polymer sample showed 31.1 mV and 110 mV, respectively. The voltage peak to peak was decreased to 4.40 mV for PVA (pure) polymer and 8.91 mV for of PVA+ZnO polymer sample. The different percentage of PVA (pure) polymer and PVA+ZnO polymer sample are 253.7% (at 50 MHz) and 102.5% (at 60 MHz) respectively. This preliminary result indicates that PVA-ZnO polymer can be used as an EM detector. Future work will be devoted to improving the fabrication technique of the composite and the weight percentage of the PVA to the ZnO.

Conclusion

In this work, single phase ZnO nanoparticles were successfully synthesized by sol-gel and self-combustion techniques. It is also concluded that the sol-gel technique has resulted in flake-like microstructure. On the other hand the self-combustion technique resulted in a rod-like microstructure. Besides, the increasing annealing temperature had resulted to an increasing crystallite size. The PVA+ZnO polymer samples showed a tremendous increase of V_{pp} indicating the role of ZnO as an EM detector.

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