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## Synthesis and Characterization of ZnO-CNTs Filled PVA Composite as EM Detector

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**Abstract:** Electromagnetic (EM) detectors in Seabed Logging require very high sensitivity and high accuracy for hydrocarbon exploration. An earnest effort was done to develop an EM detector made of ZnO-Carbon Nano Tubes (CNTs) filled composite. Single phase ZnO nanoparticles were synthesized at calcining temperature of 250 and 350°C by self combustion and sol gel methods. X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM) was done to evaluate the phase and surface morphology of the samples. XRD result shows single phase structure with major peak of [101]. The morphology of ZnO is nanospheres in shape. Based on the characterization techniques, ZnO prepared by sol gel was taken as the best sample for the detection of EM waves. Polyvinyl alcohol was mixed with ZnO nanoparticles and carbon nanotubes to fabricate the EM composite detector. It has been observed that ZnO with CNTs fillers composite detector has the ability to enhance the detection of EM waves up to 70% comparing to those without fillers.

**Key words:** Zinc oxide nanoparticles, carbon nanotubes, polyvinyl alcohol, XRD, FESEM, EM detector

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### INTRODUCTION

Detecting and assessing hydrocarbon reservoirs without the need to drill test wells has major importance in petroleum industry. Seismic methods have conventionally been used in this context, but the results can be indistinct. Another approach is to use electromagnetic sounding methods that exploit the resistivity differences between a reservoir containing highly resistive hydrocarbons and a cavity saturated with conductive saline fluids (Kong *et al.*, 2002). The Seabed Logging (SBL) method is a remote resistivity sensing method which exploits the facts that hydrocarbons are electric insulators and consequently, hydrocarbon filled reservoirs normally are more resistive than surrounding water-filled sediments (Ellingsrud *et al.*, 2002).

Currently Marine Controlled Source Electro Magnet (MCSEM) methods for the detection of hydrocarbon reservoirs have gained interest by the scientific community (Hesthammer and Boulaenko, 2005; Eidesmo *et al.*, 2002; Carazzone *et al.*, 2005; Cox *et al.*, 1986). The working principles of SBL is, firstly, a ship tows a horizontal electric dipole source (Approximately 30 m above the seafloor (Kong *et al.*, 2002; Ellingsrud *et al.*, 2002) which acts as EM transmitter close to the seabed to create large electric field. The

electric and magnetic fields are both measured and recorded by highly sensitive receivers on the seafloor. We are interested to use ZnO and carbon nano tubes as EM detector.

Zinc oxide (ZnO) is an n-type semiconductor material, wide band gap of 3.3-3.6 eV and has 60 meV excitation BE (binding energy) at room temperature (Zhang *et al.*, 2005). Zinc oxide has many applications in sensors, piezoelectric transducers, catalysts, transparent conductors and surface acoustic wave devices (Kong and Wang, 2003).

The variety of ZnO nanostructures can be fabricated by using different methods such as chemical (Non-conventional) methods such as self combustion synthesis (Ding *et al.*, 1995), hydrothermal precipitation (Wang and Shih, 1991), sol-gel technique (Tang *et al.*, 1988), glass crystallization method (Deka and Joy, 2006), chemical co-precipitation (Lucchini *et al.*, 1983), mechanical alloying (Liu *et al.*, 2004) etc. were used to fabricate the nanoparticles.

ZnO nanostructures were investigated by many researchers in different shapes such as nanorods, nanowires, nanobelts, nanotubes, nanospheres and nanocables etc. (Eftekhari *et al.*, 2006). Carbon nanotubes were discovered by Iijima (1991). Carbon nanotubes have potential applications in the fabrication of electronics

and magnetic devices due to their good electric, magnetic, thermal, mechanical and optical properties (Coolir *et al.*, 1998). Nowadays, novel carbon nanotubes based nano-devices such as transistors, probes, diodes and sensors etc. are important candidates in the electronic industry (Changqing *et al.*, 2008).

The growth of ZnO nanorods on multiwall carbon nano tubes (MWCNTs) were also reported (Changqing *et al.*, 2008). It was reported that heterostructures of ZnO nanocomposite can be used as electrode materials to increase photocurrent in photoelectrochemical cell. It was found that ZnO nanorods filled in CNT's by using wet chemical method (Qiang *et al.*, 2004). CNT's and graphite filled nanocomposite (PVDF) was reported recently by (Noorhana *et al.*, 2009). It was found that percolation threshold, at 18% of CNT's had increased the electrical conductivity of  $3.18 \text{ S m}^{-1}$  comparing to those with graphite filled nanocomposite.

The aim of this project is to design EM detector prototype potentially used for sea bed logging. ZnO nanoparticles were synthesized by using self-combustion and sol-gel techniques. The as synthesized ZnO and CNT's nanoparticles were used as fillers for the polymer composite, which was prepared using casting method. These ZnO nanoparticles and carbon nanotubes were used to prepare polymer composite by using polyvinyl alcohol (PVA) polymer. They were then used as an EM detector.

**MATERIALS AND METHODS**

The starting materials  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{HNO}_3$  solution was used to synthesize zinc oxide nanoparticles. ZnO nano particles were prepared by employing sol-gel and self-combustion techniques. The zinc nitrate was dissolved in the aqueous solution of 50 mL of nitric acid. The solution was stirred at 250 rpm for 24 h and was allowed to combust on the hot plate stirrer with gradual heating after 40 min. The sol was combusted at  $110^\circ\text{C}$ . The combusted material was dried in the oven at  $110^\circ\text{C}$  for 24 h and dried samples were crushed for 2 h to obtain the fine particles. After crushing the samples were annealed at  $250$  and  $350^\circ\text{C}$  for 2 h. The sol gel method requires longer stirring time (1 week) and lower stirring temperature,  $80^\circ\text{C}$ .

The phase and the crystal structure of the as-prepared samples were identified by using X-Ray Diffraction analysis (Bruker D8 advance). Field Emission Scanning Electron Microscope (SUPRA 35VP) was used to observe the surface morphology of the samples. PVA composite was used as a binder for the samples (ZnO SC250, ZnO SC350, ZnO SG250 and ZnO SG350).

To prepare the composite detectors, 1.2 g of PVA was mixed with 22.2 mL of deionised water in the beaker. The mixer was heated at  $60^\circ\text{C}$  on the heating mentle. 0.1 mg of ZnO and also 0.1 mg of carbon nano tubes were added into PVA mixer and fabricate ZnO, CNTs and PVA composite to get high detection of EM waves. The EM composite detectors were connected to a holder as shown in Fig. 1. The dimension was also given in Fig. 1.

Figure 2 shows our interest to study the configurations of the EM detectors. Configuration 1 gives AB connection and configuration 2 gives CD connection, both in parallel. Copper wire was used as a contact to the detectors. Model RX01 is the PVA composite detector without additives. Model RX02 represents PVA with ZnO composite detector. Model RX06 is the detector filled with the both ZnO and CNTs. The ZnO and CNTs as additive were used to perform better enhancement in EM detection.

The EM signal is generated by a function generator, Goodwill INSTEK GFG-8250A (1 Hz to 6 MHz). A Pico Log ADC-16 data logger offers high resolution (16 bits sign) and is capable of detecting signal changes as small as

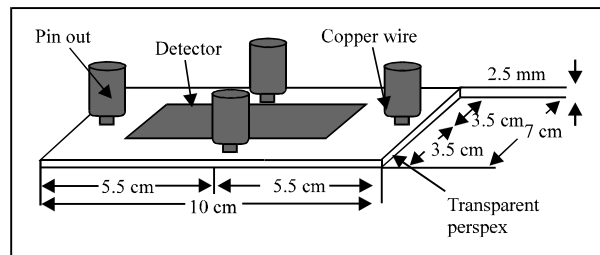


Fig. 1: Size and dimensions of detector holder

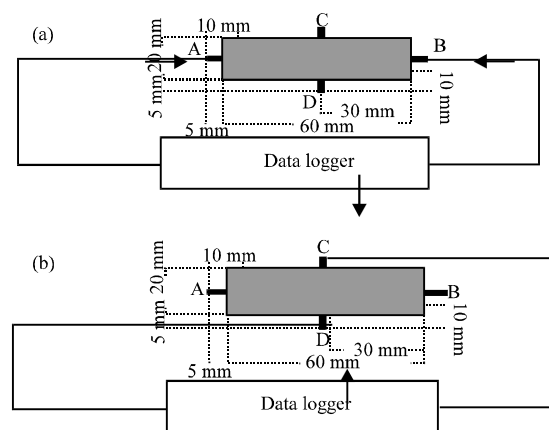


Fig. 2: (a) Configurations of detector 1 and (b) configurations of detector 2

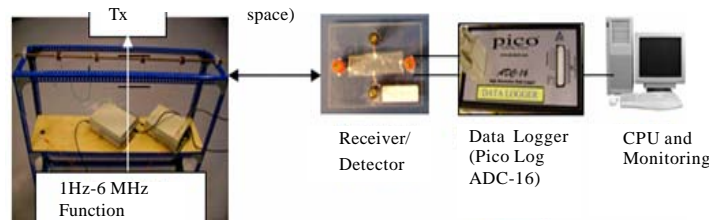


Fig. 3: Experimental setup for EM wave detections

40 μV. The experimental setup for EM detection is shown in Fig. 3. We used aluminum based transmitter to produce the EM waves.

### RESULTS AND DISCUSSION

X-ray diffraction patterns of zinc oxide which was calcined at 250 and 350°C prepared by self combustion method and sol gel methods are shown in Fig. 4. XRD patterns were indexed by using standard JCPDS card no (89-1397) for ZnO. The XRD patterns shows that zinc oxide samples both prepared by sol gel and self combustion have single phase structure and shows good crystallinity at the calcinations temperature of 350°C (Liu *et al.*, 2004). The crystallite size has been measured from X-ray diffraction patterns by Debye Scherer equation (Eftekhari *et al.*, 2006).

$$D = \frac{K \lambda}{\omega \cos \theta} \quad (1)$$

Where λ is the incident ray wavelength, θ is the Bragg diffraction angle and β is the full width at half-maximum (FWHM) of the major peak.

The calculated crystallite size is shown in Table 1 and the results show that all samples have crystallite size in nanometer range. It has been observed that as calcination temperature increases, crystallite size also increases and all samples have hexagonal structure.

Field Emission Scanning Electron Microscopy (FESEM) was used to evaluate the morphology and grain size of all the ZnO samples. Figure 5b-e show FESEM micrographs for ZnO calcined at 250 and 350°C. ZnO nanoparticles that were prepared by self combustion method resulted fine grain morphology. The grain size also increase as the calcination temperature increases from 250 to 350°C. The grain size varies between 35 to 80 nm which is in consistent with the crystallite size calculated from XRD the graphs (Table 1). Figure 5a exhibits the CNTs morphology with the diameter ranges from 30-90 nm. It is clear that these CNTs have high aspect ratio.

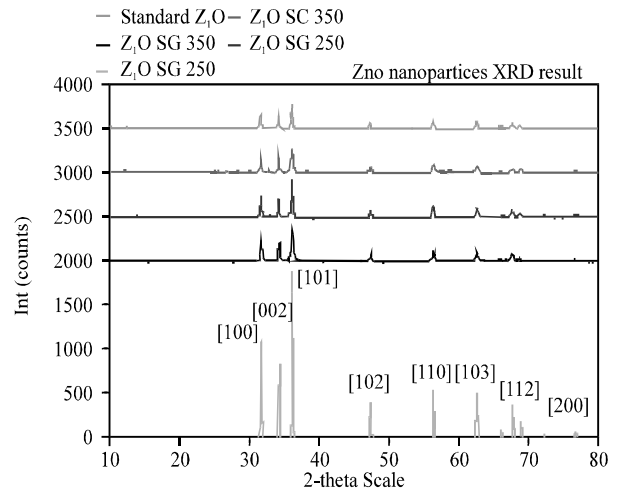


Fig. 4: X-ray diffraction patterns of ZnO standard and ZnO calcined at 250 and 350°C prepared by self combustion and sol gel methods

Table 1: XRD results for samples prepared by self combustion and sol-gel

Method	ID	FWHM	Crystal- lite size (nm)	d-spacing
Self combustion	ZnOSC 250	0.230	45.26	2.473
	ZnOSC 350	0.215	49.45	2.476
Sol gel	ZnO SG 250	0.278	38.19	2.476
	ZnO SG 350	0.245	44.21	2.479
Conventional	ZnO Standard	0.113	93.84	2.476

Table 2 exhibit the elemental analysis of all the ZnO samples. From the periodic table, the weight % of zinc is 80.34% and oxygen has 19.65%. The atomic percentage for ZnO should be 50% of Zinc (Zn) and 50% of Oxide (O). The EDX results are in accord with theoretical values as shown in Table 2.

Based on the FESEM images and X-Ray Diffraction patterns of all the ZnO samples, it was concluded that samples prepared by sol gel method has good morphology and small grain size.

Figure 6 and 7 give voltage (peak to peak) of the three EM detectors connected according to configuration 1 and 2, respectively. From Fig. 6 we can see that PVA

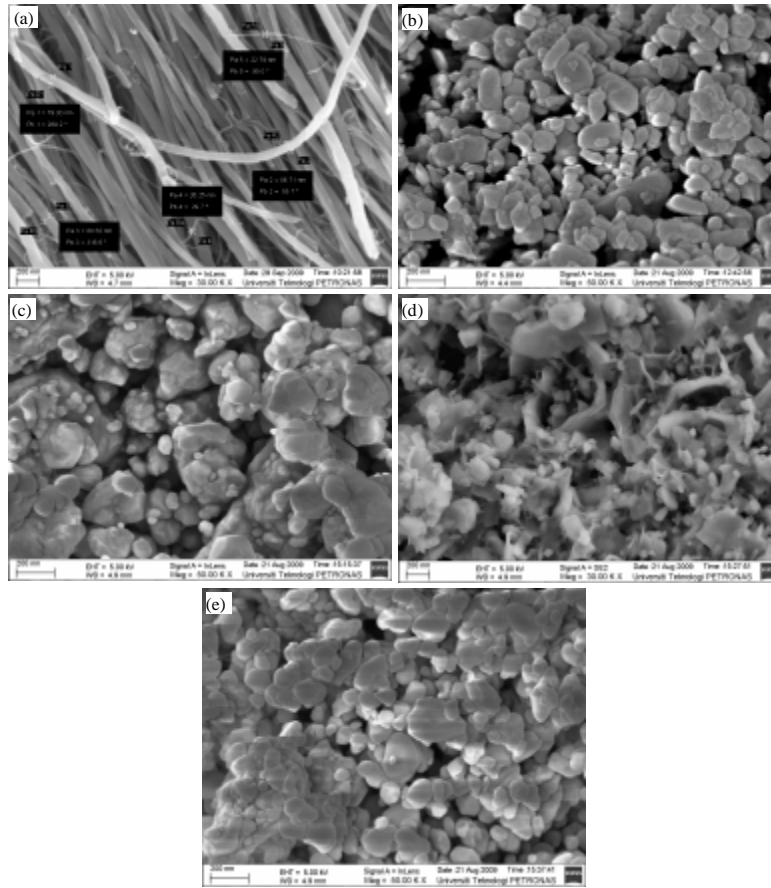


Fig. 5: Scanning Electron Microscopy results for (a) Multiwall carbon nano tubes (b) ZnO calcined at 250°C by self combustion, (c) ZnO calcined at 350°C by self combustion, (d) ZnO calcined at sol gel methods and (e) ZnO calcined at sol gel methods

Table 2: Elemental analysis for zinc oxide samples calcined at 250 and 350°C prepared by self combustion and sol gel method.

	ZnO SC 250		ZnO SC 350		ZnO SG 250		ZnO SG 350	
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	Atomic -%Weight		Atomic -%Weight		Atomic -%Weight		Atomic -%Weight	
O	20.16	50.78	23.59	50.79	19.26	49.36	21.28	52.49
Zn	79.84	49.22	76.41	49.21	80.74	50.64	78.72	47.51

composite filled with ZnO nanoparticles prepared by sol gel method gives higher (18.67%) EM detection than samples prepared by self combustion method (5.33%).

Similarly, Fig. 7 shows that PVA filled with ZnO prepared by sol gel give higher (19.17%), whereas (13.17%) was observed for the samples prepared by self combustion method. From the above results it has been concluded that in both configurations ZnO samples prepared by sol gel method shows enhancement of EM signal than ZnO prepared by self combustion method and PVA composite without ZnO fillers.

Besides using an oscilloscope, we also used a data logger to measure the EM waves. Figure 8 shows the results of PVA, PVA composite filled with ZnO and PVA composite filled ZnO with CNT's.

From Figure 8 we can see that ZnO-CNT's PVA composite (Model RX06) shows 0.29 % more in detection than ZnO PVA (Model RX02) composite. The PVA composite (Model RX01) without any fillers gives the lowest detection. It should be noted that we conducted this experiment using configuration 1. Model RX06 was found to show better EM detection. This is due to the fact that ZnO-CNT's filled composite gives better connectivity. It is speculated the high aspect ratio of the CNT's (Fig. 5 a) had given the better detection. The well dispersed ZnO-CNT's fillers have higher induced voltage hence better pathway resulting to the improved detection (Noorhana *et al.*, 2009). It should also be noted ZnO nanoparticles have large surface area (small grains) and carbon nanotubes fillers act as bridge between the

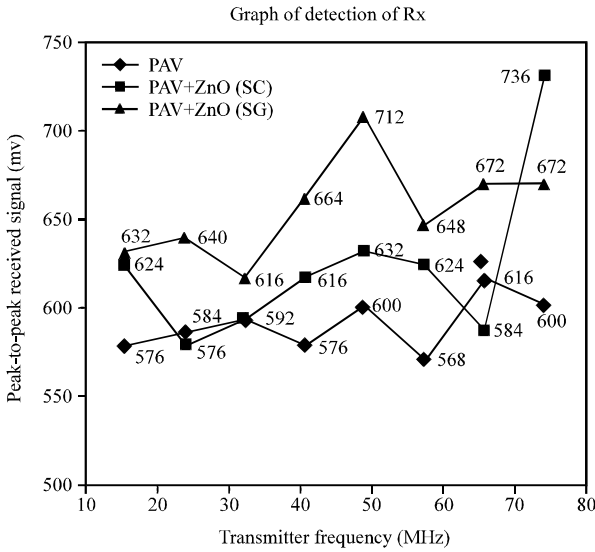


Fig. 6: PVA, PVA with ZnO (SC) and PVA with ZnO (SG) for configuration 1

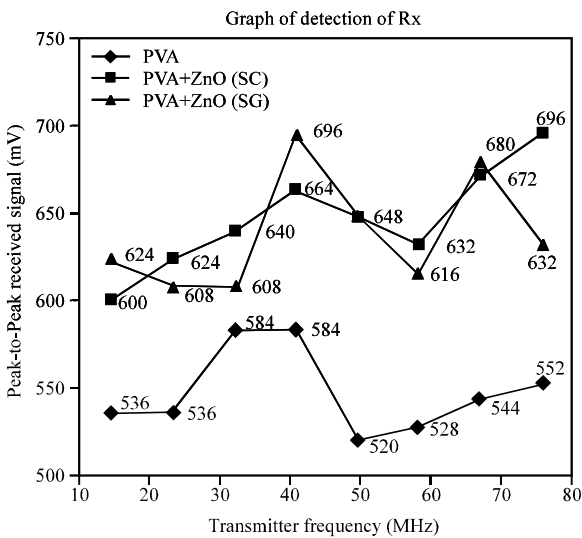


Fig. 7: PVA, PVA with ZnO (SC) and PVA with ZnO (SG) for configuration 2

ZnO nanoparticles in PVA polymer composite. Due to this, ZnO with CNT's fillers in PVA gives better detection as compared to PVA polymer composite.

Figure 9 show results for the different weight ratios of carbon nano tubes and ZnO in PVA composite detector. From the results it can also be observed that an increased in the ratio of carbon nano tubes and ZnO caused increased of % EM detection. It was observed that the EM detection has increased up to 70% by increasing additives (ZnO and CNT's).

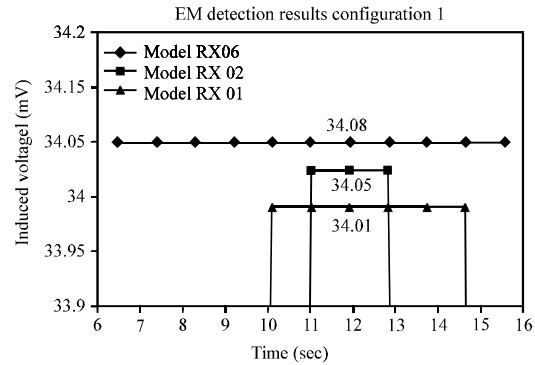


Fig. 8: EM detection results of PVA (RX 01), ZnO PVA (RX 02) and ZnO-CNT's PVA (RX 06)

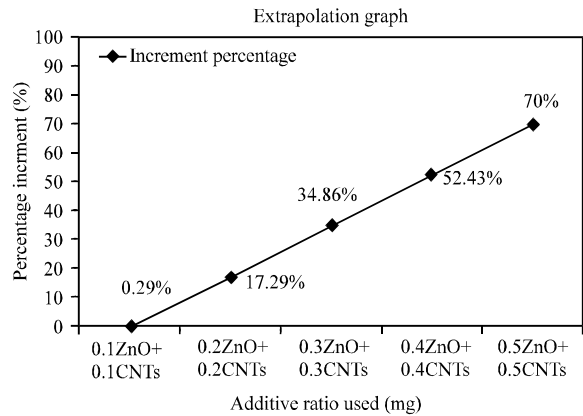


Fig. 9: Different ratios of CNT's and ZnO in PVA polymer composite

### CONCLUSION

ZnO nanoparticles were successfully synthesized by sol-gel and self-combustion techniques. X-Ray diffraction results reveals that crystallite size increases as calcination temperature increased from 250 to 350°C. Scanning electron microscopy results shows that ZnO prepared by sol gel method has better morphology and are spherical in shape. The elemental analysis of all synthesized samples indicates high purity of samples. EM detectors were successfully fabricated by using ZnO and CNT's filled polymer composite. It was concluded that both CNT's and ZnO have improved the detection by 70% comparing to PVA polymer composite without fillers.

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