

CHAPTER THREE

EXPERIMENTAL SETUP AND MWCNT/PEO, MWCNT/PVA AND MWCNT/PVA/ZnO COMPOSITES FABRICATION TECHNIQUES

3.1 Introduction

In this chapter, we describe the experimental setup. This includes fabrication of composites, characterization and application of composites and various compounds as methanol sensors. The fabricated composites are MWCNT/PEO, MWCNT/PVA and MWCNT/PVA/ZnO. Subsequently, the composites were tested by methanol vapor and resistance was measured by changing the composites at methanol composition from 10 to 50 at steps of 10 (10, 20, 30, 40, and 50) while the concentration kept constant at vol% at room temperature. Eventually, we investigated and analyzed man-sized of ZnO utilizing ball milling by X-ray diffraction technique, various peaks of MWCNT/PVA and MWCNT/PVA/ZnO by Fourier Transform Infra-red Spectrum (FTIR) technique and morphology of these samples by Scanning Electron Microscopy (SEM) have been studied.

Section 3.2 presents the used materials in the experiment and the sample preparation respectively. The analytical techniques are discussed in Section 3.3. Section 3.4 describes the instruments which are have been used along with the experimental setup. The

measurements calculations of the sensing properties are found in section 3.5. The preparation of nano-sized ZnO by ball milling is described in section 4.2.

3.2 Fabrication of Composites

Multiwall Carbon Nanotubes (MWCNTs)

Specimens were made using commercially available MWCNT purchased from Chengdu Organics Chemical Co. Ltd, China. These specimens were prepared by chemical vapor deposition. The tube diameter ranged from 10 to 30 nm, the tubes length range from 5 to 15 μm and the purity is 90%.

Polyethylene Oxide (PEO)

High Molecular Weight Polyethylene Oxide (PEO) is white, hydrophilic powder (average $M_w \sim 1,000,000$, powder) was purchased from sigma-Aldrich to be used as matrix material because of its good solubility in water.

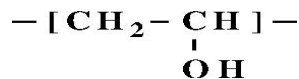
HMWPEO has a linear structure with high crystalline and density. This makes it stiff and strong polymer with melting temperature of 64°C and low glass transition temperature of 60°C [2]. The chemical formula of PEO is $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n$ [4] .

Sodium Dodecyl sulfate (SDS)

Sodium Dodecyl sulfate ($C_{12}H_{25}NaO_4S$) is an ionic surfactant that is used as a dispersing agent to lower the surface tension between MWCNT and water. It can form stabilized dispersion, since it can prevent reaggregation of nanotubes.

Polyvinyl Alcohol (PVA)

Polyvinyl alcohol (PVA) is a water-soluble and white 87-89% hydrolyzed powder (Typical average $M_w \sim 146,000-186,000$) was purchased from Sigma-Aldrich. It was used as the matrix material because of its good solubility in water. PVA has a linear structure with high crystallinity and density, high melting temperature and high glass transition temperature, the glass transition temperature and melting point of PVA are 85°C and 230°C respectively. The chemical structure of PVA is



Triton X-100

Triton X-100 was purchased from Sigma-Aldrich. It is a nonionic surfactant which has a hydrophilic polyethylene oxide group. It was used as dispersion of carbon materials for soft composite materials and has a high boiling point. Some properties of Triton X-100 are tabulated in table 3.1

Table 3.1: - Displays some properties of triton.

Formula	$(C_2H_4O)_n C_{14}H_{22}O$
Melting point	6°C
Boiling point	>200°C
Solubility in water	Soluble
Batch	118 KO160

Zinc Oxide:

Zinc oxide is an n-type semiconductor of wurtzite structure with high direct bandgap of ~3.37eV at room temperature [6]. It usually appears as a white powder, has a high refractive index, high thermal conductivity and good transparent. Some properties of zinc oxide are tabulated in table 3.2.

Table 3.2: - Displays some properties of zinc oxide.

Formula	ZnO
Melting Point	1975°C (decomposes)
Boiling Point	236°C
Band gap	3.37eV (direct)
Refractive index	2.0041
Solubility in water	0.16gm/100ml (30°C)

Methanol

In the current work, we choose an absolute Methanol to investigate the sensing properties of the fabricated composites. Methanol is the simplest of alcohols, having only one carbon atom [6], and is completely miscible in water. Methanol (CH₃OH), (also called methyl alcohol) is a clear, colorless, volatile liquid with a faint alcohol-like odor and it is

difficult to detect at concentrations below 10ppm, so it is important to find new and more efficient methanol sensors based on novel materials. Methanol easily dissolves in other alcohols and chlorinated hydrocarbons, but has limited solubility in diesel fuel and aliphatic hydrocarbons [5]. Some properties of methanol are summarized in table 3.2.

Table 3.3: - Displays some properties of absolute Methanol.

Structure	$ \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array} $
Molecular formula	CH ₃ OH
Density	0.7918 g/cm ³
Dipole moment	1.69 D (gas)

3.2.1 MWCNT/PEO

Two groups of MWCNT/PEO composite were fabricated:

Group (1): - Unaligned composite with SDS.

Group (2): - Unaligned composite after removing SDS.

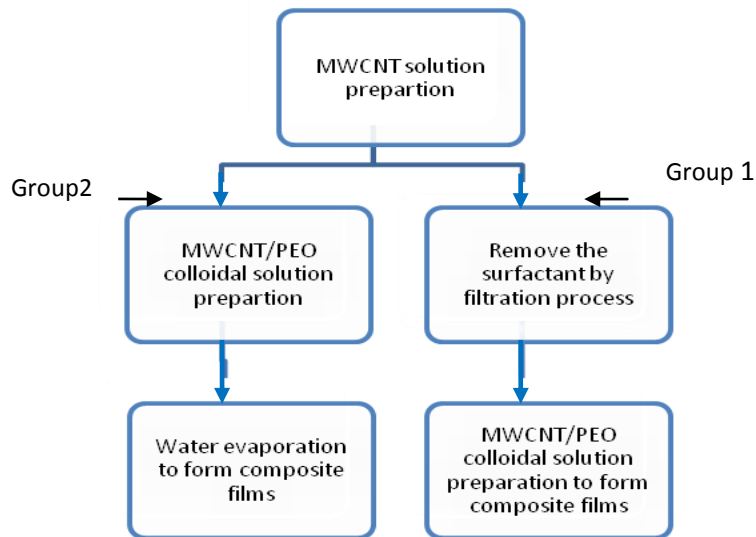


Figure 3.1: - Shows a schematic diagram for the preparation of two groups of composites.

The CNT/HMWPEO nanocomposite was fabricated using solution casting method. In this experiment we choose water as a solvent and SDS as surfactant.

- 1- 1g SDS added to 50 ml D. I. water. MWCNT solution prepared by mixing 1g MWCNT with SDS solution and stirred for one hour. Ball milling technique to dispersion MWCNT has been utilized.
- 2- SDS solution containing 1g MWCNT was agitated in an ultrasonic for one hour to obtain stable suspension of MWCNT in water.
- 3- PEO solution prepared by dispersion in 50ml. D. I. water by magnetic stirrer for 1 hour at 140°C. The MWCNTs concentration needed in PEO was calculated to

obtain a range of loading between 0.99 wt% to 9wt% CNT in the composite films. Each concentration of the dilute MWCNT was then added to the polymer colloidal solution and stir for 1 hour. The resulting outcome was poured into a casting frame. For unaligned nanotube composites, removing the solvent was achieved by evaporation of water at room temperature for several days.

Table 3.4 shows details of materials and facilities used for experimental setup of composite preparation.

Table3.4: - Displays facilities and materials for the experimental setup.

Materials/facilities	Quantity/Model
Multi walled carbon nanotube (MWCNT)	1g
Polyethylene Oxide (PEO)	1g for each loading of CNT
Sodium Dodecyle Sulfate (SDS)	1g
Magnetic stirrer	Barnstead Thermolyne
Ball milling machine	Pulverisette 7
Steel grinding balls	15 balls in each bowl

MWCNT Sheet Preparation

As described above, SDS aqueous solution was prepared and stir with 1g of MWCNT. Afterward, the solution was agitated using ball milling technique (Pulverisette 7) for one hour at 200rpm. A certain concentration of CNT was spread on filter paper (Double Rings, 9.0cm, 102 Qualitative) and left it to dry at room temperature. This resulting in deposited nanotube on the top of the filter paper and the residual water passed through the pores of the paper. Figure 3.2 shows the filter paper before and after addition of the

MWCNT solution. After drying, the paper was cut to desired dimensions. The dimensions of the prepared paper were 2cm length and 0.5 cm width. The MWCNT paper was painted with silver paint to make good electrical contacts.

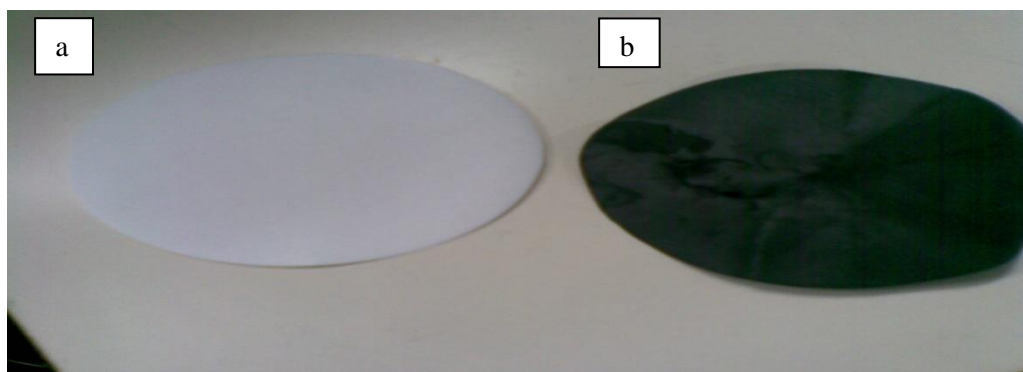


Figure 3.2: - Depicts the photograph of (a) filter paper, (b) filter paper deposited with MWCNT/PEO composite.

Filtration Process

The MWCNT solution was filtered utilizing filter paper (9.0cm, 102 Qualitative) with the purpose of cleaning it. The solution passed through the filter to be collected in a flask. After all solution passed through the filter, D. I. water was added to wash the SDS many times. The residual nanotube was collected from the filter and then mixed with 100ml D. I. water and stirred for one hour.

3.2.2 MWCNT/PVA

Composite Fabrication:

The CNT/PVA nanocomposite was fabricated using solution casting method. In this experiment, water as a solvent and triton X-triton as the dispersing agent of MWCNT have been chosen.

MWCNT Solution Preparation

MWCNT solution was prepared by mixing 0.7g triton X-100 with 50ml D. W. with 0.35g MWCNT. The MWCNT solution has been kept in ultrasonic for 30 minutes. This resulted in homogeneous dispersion of the MWCNT in the triton X-100 solution.

MWCNT/PVA Solution Preparation

1g PVA was dissolved in 50ml D. I. water putting in use a magnetic stirrer for 2 hours at a fixed temperature of 100°C. The mixture was left until the PVA is totally dissolved in water. The MWCNTs concentration needed in PVA was calculated to obtain a range of loading between 1, 2, 3, 4 and 5%wt CNT in the composite films. Each concentration of the dilute MWCNT was later added with polymer colloidal solution and stir for 2 hours. The composites were dried to form films by leaving the solution in petri dishes at room temperature for several days. The composite solutions with different MWCNT loading are shown in Figure 3.3



Figure 3.3: - Shows MWCNT/PVA colloidal solutions at different loadings.

3.2.3 MWCNT/PVA/ZnO Solution Preparation

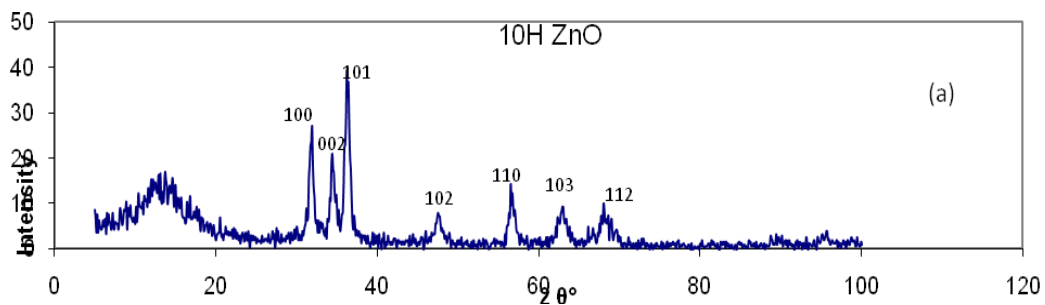
0.01g ZnO was dispersed in D. I. water by magnetic stir for 2 hours at a fixed temperature of 100°C. The mixture then added with 2ml of MWCNT/PVA solution, followed by putting them in magnetic stirrer for 2 hours. This process repeated for 0.02g, 0.038g, 0.04g and 0.05g to obtain five different composites. The composites were left to dry at room temperature.

3.3 Preparation of Nano-sized ZnO by Ball Milling

Nano-sized ZnO powder prepared by ball milling was used as additive in MWCNT/PVA/ZnO composite. The phase structure of ZnO powder and estimated average crystal size were studied using x-ray diffractometer (XRD) model [XRD, siemens D-500]

by using copper-monochromatized $\text{CuK}_{\alpha 1}$ radiation ($\lambda=1.54\text{\AA}$) under the accelerating voltage of 40kv and a current of 40mA. It is capable of producing high-intensity CuK_{α} radiation and optimized operating conditions of scanning rate of $0.04^\circ/\text{s}$ in the 2θ range from 0° to 110° .

Figure 3.4 shows the XRD spectra obtained from ZnO ball milled for 10hrs (Figure 3.4a), 20hrs (Figure 3.4b), 30 hrs (Figure 3.4c). In all the spectra the peaks can be assigned to (110), (002), (102), (103) and (112) hexagonal wurtzite structure of ZnO [6] as marked figure 3.4a .The pattern at 10hrs milled ZnO powder shows a series of strong and narrow peaks characteristic for low quality ZnO crystals (figure 3.4a). With increasing the milling time, the diffraction peaks become ordered and their relative intensity increases, as shown in Figure 3.4b, 3.4c [7]. Broad diffraction peaks from (100), (002) and (101) corresponding to ZnO, were observed, accordingly, the diffraction peaks can be indexed in terms of the structure of crystalline ZnO. This result indicates that ZnO prepared by copper-monochromatized radiation for 10hrs, 20hrs and 30hrs were in a relatively crystalline phase [8].



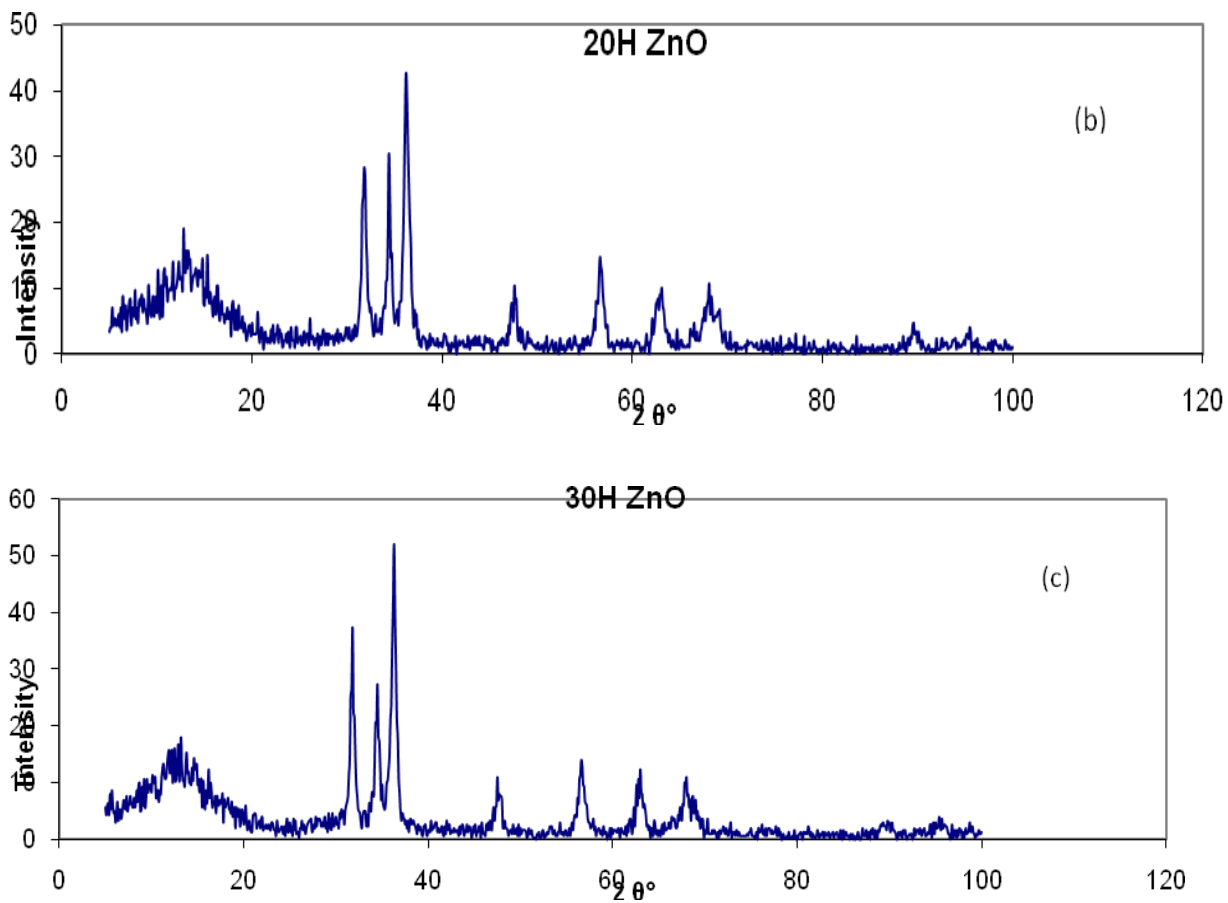


Figure 3.4: - XRD patterns of ZnO ball milled for (a) 10 hours (b) 20 hours (c) 30 hours.

Figure 3.5 shows the high resolution scan of the (100) peak of ZnO ball milled for 10 hours (figure 3.5a), 20 hours (figure 3.5b) and 30 hours (figure 3.5c) where the 2θ value about 31.6° .

The mean grain size (d) of the ZnO sample, were calculated using Scherer's equation:

$$d = \frac{k\lambda}{\beta \cos \theta} \quad (3.1)$$

Where,

β is the measured broadening of a different line peak, full width at half its maximum intensity in radians,

$k=1$,

λ is the X-rays wavelength (0.154056nm) and

θ is Bragg diffraction angle.

By fitting various peaks to Scherer's equation, crystallite size values 12, 13 and 11nm. The results are presented as a function of time [5]. The results are plotted in Figure 3.6. The crystallite size showed almost no change with time from 10 to 30 hours milling time. It seemed that 10 hours milling was enough to reach the limit of particle size reduction in our milling system.

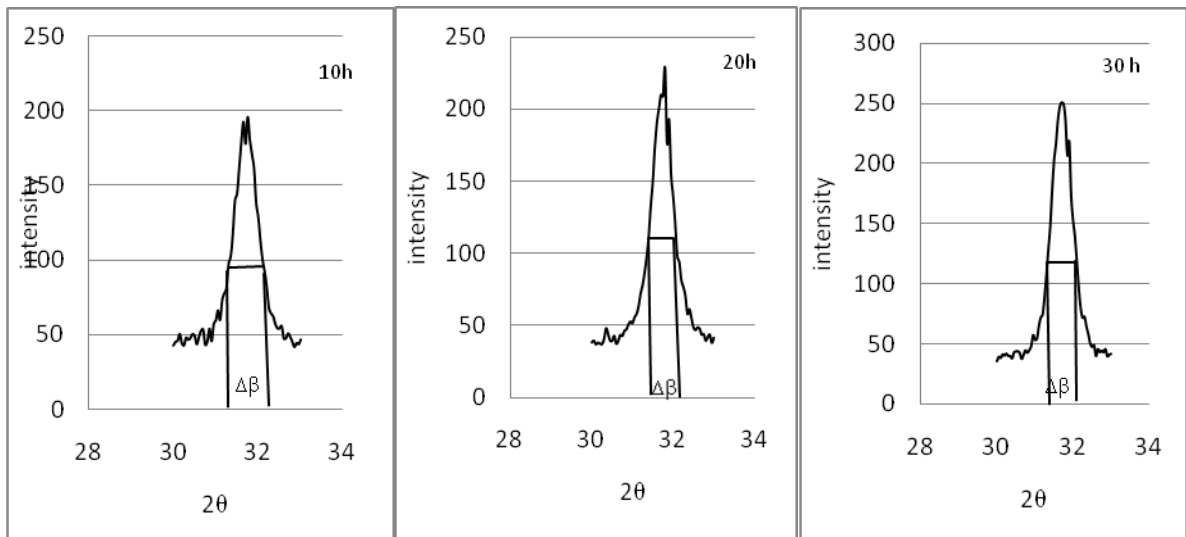


Figure 3.5: - Illustrates peaks of XRD for ZnO at different time and show full width at half its maximum intensity.

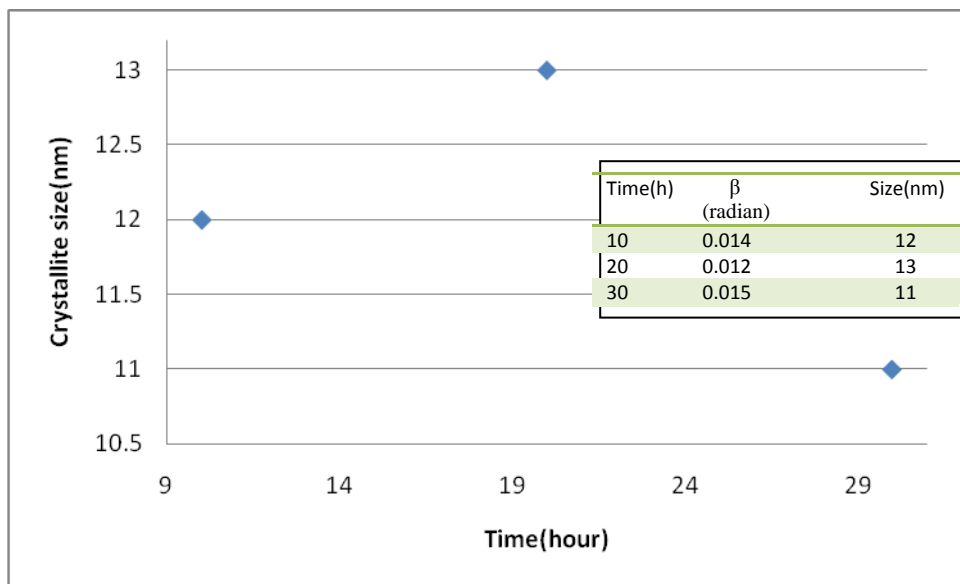


Figure 3.6: - Crystallite dimensions of ZnO sample with milling time.

3.4 Characterization

The crystal structure of ball milled ZnO was analyzed by using XRD (Siemens D-5000) with $\text{CuK}_{\alpha 1}$ X-ray beam at $\lambda=1.5408\text{\AA}$. Figure 3.7 is an example of ZnO powder response to XRD spectra. While the samples surface morphology were observed using a scanning electron microscope (SEM) model LEICAS440 (PAMC-00081). The FTIR spectra were recorded on a VICOLET IS10 FTIR instrument (brand thermo scientific, company research instruments).

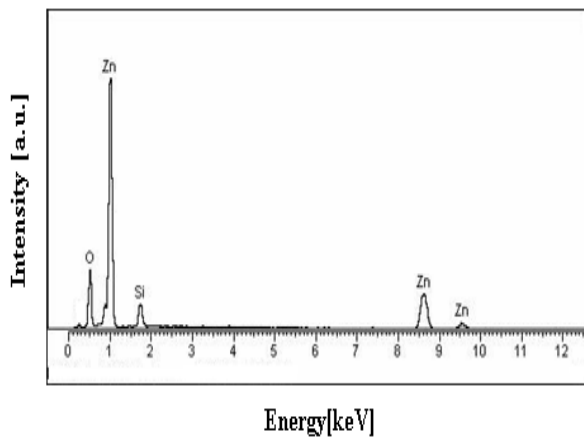


Figure 3.7: EDX spectrum of as-synthesized ZnO nanostructures.

3.5 Experiment Setup Application as Gas Sensor

The chemical sensing properties of the MWCNT/PEO on filter paper, MWCNT/PVA and MWCNT/PVA/ZnO were measured by comparing the electrical resistance of the samples under methanol vapour and air ambient. The measurements were

carried out at room temperature. The samples dimensions were (2cm length and 0.5cm width). Moreover, the flow rate of air through the methanol solution was 40sccm.

The same way is repeated on MWCNT/PVA and MWCNT/PVA/ZnO, but here we will use methanol vapor flow-rate of 40sccm.

Figure 3.8 shows schematic diagram of the measuring system. The pump (model DOA-P504-13N) was connected with flow meter (model Coleparmer (1-800-323-4340) used to control the methanol vapor flow-rate which is connected with the flask containing methanol liquid. The sample was connected with the flask (1000ml) and the digital multi-meter (model Thander Thurby 1604) to measure the resistance of a dc voltage bias of 1V. The measurement was conducted alternately switching on and off the pump so that the sample was alternately exposed to air and methanol vapor. The total exposure time was 10 minutes.

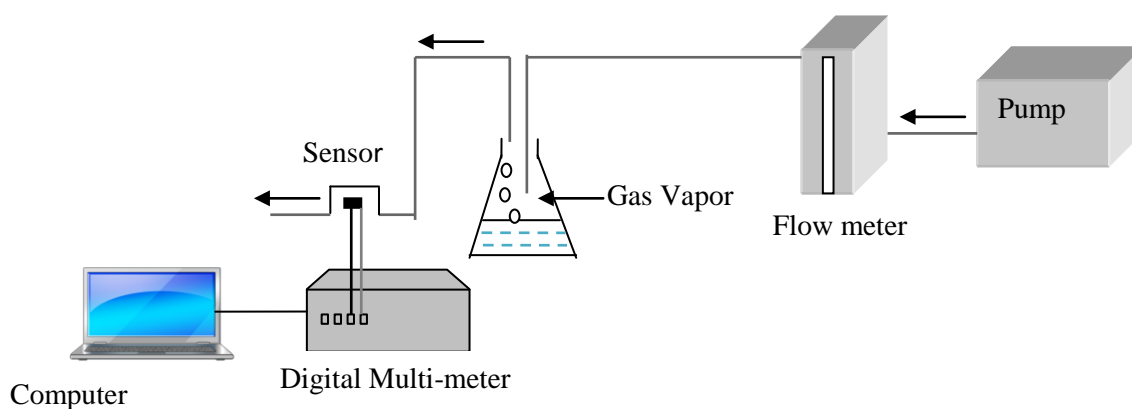


Figure 3.8: - Experimental setup of the measuring system.

3.6 Resistance Measurement

The change of resistance is calculated by dividing the actual resistance by the initial value measured in air ambient.

The sensitivity S is calculated using the following equation:

$$S = \frac{R_g - R_o}{R_o} \times 100 (\%) \quad (3.2)$$

Where R_g is the resistance of methanol and R_o is the resistance of air.

The response time of the sample is the time needed to change the resistance from air ambient to methanol. Figure 3.9 is an example of a sensor response to methanol vapor using our measurement set up.

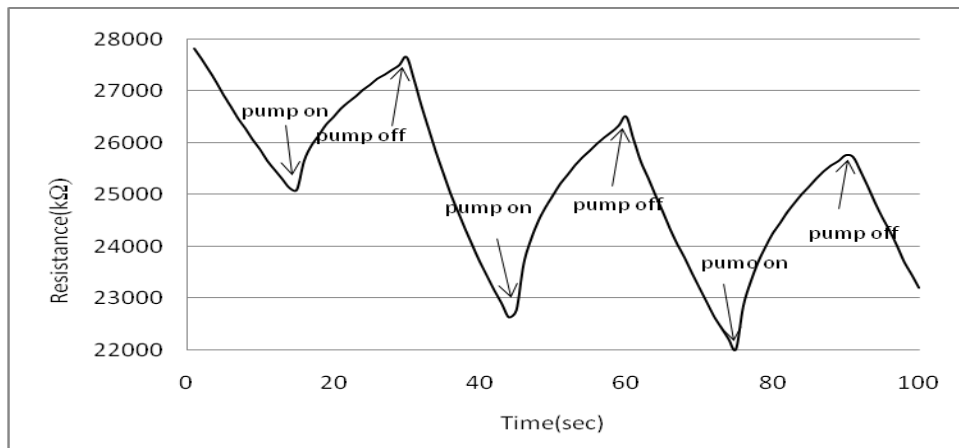


Figure 3.9: - Resistance change measured at 16.7 vol.% for various times.

References

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