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EFFECT OF MOLARITY ON GROWTH OF NANORODS ON WIRE VIA SONOCHEMICAL METHOD

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ABSTRACT

In this work ZnO nanorods were successfully grown sonochemically on several types of wires, (silver (Ag), nickel (Ni), copper (Cu) and tungsten (W)) using zinc nitrate hexahydrate and hexamethylenetetramine (HMT) solution at different molarity without template or surfactant assistance. The SEM morphology showed the nanorods are non-directional as compared to those grown on semiconductor substrate. Nonetheless, XRD indicated that ZnO structure follows the hexagonal wurtzite structure with the preferential growth in the (002) direction. Different densities and sizes of nanorods were observed using different concentrations. This study provides a novel yet efficient approach for the synthesizing of ZnO nanorods.

Keywords: Zinc oxide (ZnO); nanorods, sonochemical method;

INTRODUCTION

ZnO is a key material with novel applications in the field of nanoscience and nanotechnology. Zinc oxide (ZnO) is a semiconductor material which is extensively researched due to its potential to be used in variety of applications such as photo-detectors, light emitting diodes, piezoelectric transducers, chemical or biosensors, solar cells, actuators etc. [1]. There are two ZnO crystalline phases which is the hexagonal wurtzite and cubic crystal. The three major crystalline structures are wurtzite, zinc blend and rock-salt. The most sought after is the ZnO wurtzite hexagonal phase as it has diverse morphologies, properties and applications other than its excellent physicochemical properties [2, 3]. Generally the possible growth mechanism of ZnO nanorods can be divided into two parts: nucleation and growth. During nucleation, small molecules join together forming particles which combines with one another growing to a certain thickness. The possible growth path for ZnO crystal is the Ostwald ripening process [4]. This phenomenon states that “the growth of larger crystals from those of smaller size which have higher solubility than the larger ones” [5]. For the growth of ZnO, after the period of nucleation and incubation, a crystallite will form into a three dimensional object, with well-defined and low crystallographic faces. A few known 1D ZnO nanostructures with different morphologies that have been synthesized and characterized are such as rods, wires, tubes, belts, needles, tips etc. [6]. There have

been a few methods documented on the fabrication of ZnO nanorods such as hydrothermal, vapor-liquid-solid (VLS), pulsed laser deposition (PLD) and metal organic vapor-phase epitaxy (MOVPE) method [1]. Some of this method are time consuming and requires certain growth conditions such as lengthy growth period, elevated temperature, and specific pressure. This work focused on the fabrication of ZnO nanorods using sonochemical method. The sonochemical reaction is based on acoustic cavitation which involves in the formation, growth and implosive collapse of bubbles in a liquid medium.

Research by Nayak et al. (2010) has presented on growth of ZnO nanowire using sonochemical method. The growth of ZnO nanorods can be promoted through an intermediate product of zinc hydroxide [7]. The growth of ZnO nanorods is indicated through the following chemical reaction:

$$(CH_2)\,6N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHO. \quad (1)$$
$$NH_3 + H_2O \rightarrow NH_4 + OH^-. \quad (2)$$
$$Zn(NO_3)6H_2O \rightarrow Zn^{2+} + 2NO^{3-}. \quad (3)$$
$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2. \quad (4)$$
$$Zn(OH)_2 \rightarrow ZnO + H_2O. \quad (5)$$

Hu et al. (2004) has demonstrated the applicability of sonochemical method in producing free standing ZnO rods [8]. However, there is no report about using this method in growing ZnO nanorods directly on wire without seeding method. As such, the aim of this work is to produce a fast and efficient method for the growth of ZnO nanorods in one-pot synthesis method under ambient conditions using various thin wires (Ag, Ni, Cu and W) as template for the growth of the nanorods.

EXPERIMENTAL

ZnO nanorods were grown by ultrasonic irradiation on a thin wire (Ag, Ni, Cu & W) with diameter of 100 µm. The wires were cut in lengths of 3 cm and cleaned with ethanol and rinsed with deionized water and then dried in air at room temperature. An aqueous solution of zinc nitrate hexahydrate, [Zn(NO3)2.6H2O 99 %] and hexamethylenetetramine, HMT, [(CH2)6N4, 99 %] purity was stirred with a magnetic stirrer bar at 350 rpm for 10 minutes yielding a clear solution. ZnO nanorods were grown by immersing wire in the aqueous solution and sonicated at optimized parameter (47 % of the maximum amplitude of the 20 kHz ultrasonic probe for 30 minutes). The illustration is shown in Figure 1. The wire was then rinsed with DI water and left to dry under normal ambient. The effect of concentration was investigated using Zn(NO3)2.6H2O and HMT with equimolar concentrations of 0.005 M, 0.01 M and 0.05M while keeping other variables constant. All reagents used were of analytical grade and used without further purification.

The morphologies were observed using Field Emission Scanning Electron Microscopy (FESEM) (NOVA Nanosem 45) and High Resolution Transmission Electron Microscopy (HRTEM) (TEM Libra 120). The crystallinity and phase of rods were inspected using X-ray Diffraction (XRD) (D/max-IIIC X-ray diffractometer).

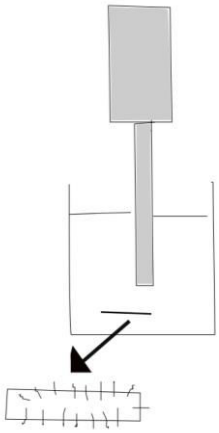

Figure 1: ZnO nanorods grown on metal wire through sonochemical method (ultrasonic probe)

SEM micrograph in Figure 2 shows the synthesized ZnO nanorods morphology, structure and size with increasing concentrations. The concentration of $Zn(NO_3)_2$ and HMT were found to directly influence the morphology of ZnO products. The shape of ZnO changes from needle-like to rod shaped as the concentration increases. The surface of the rods also appears to be smooth, clean and hexagonal shaped. This shows that the shape and size of ZnO nanorods can be controlled depending on the concentration of zinc nitrate hexahydrate and HMT. It is important to maintain the ratio of reagents zinc nitrate hexahydrate to HMT at 1:1. This is to ensure the growth of anistrophic ZnO nanoparticles. Work by Vayssieres (2003) stated that the diameter of rods changes linearly according to the change of precursor concentration [9]. The rods are seen to have different length and diameters as shown in Figure 3. The average diameters of the rods are in range of 50-150 nm and the length in the range of 250 nm- 1 µm. Longest ZnO nanorod is observed grown on Ni wire at concentration 0.005 M and 0.01 M. At concentration 0.05 M the length and diameter of nanorods are observed to be smaller in diameter and shorter in length on all four wires compared to the other two concentrations. The function of HMT in the reaction is also to limit horizontal growth of ZnO hexagonal crystal and promote growth along the vertical c-axis [10]. From the SEM images, it could be observed clearly that the shapes of the ZnO nanorods are dependent on the concentration of zinc nitrate hexahydrate and HMT. . As the growth of the nanorods increases with precursor concentration, it could be observed that the nanorods grown show no preferential growth direction. As the surface of the wire has uneven surface roughness, it could be hypothesize that this characteristic might have led to disorder orientation growth of the nanorods. Surface roughness directly impacts the

growth orientation of ZnO nanostructure as reported by a research by Breedon et al, (2008) whom had grown ZnO nanostructures on various subsrates [11]. Figure 4 shows the TEM image of typical ZnO nanorods. The sample was ZnO grown on Ag wire at 0.05 M concentration. Only one sample of the highest concentration was used to prove the presence of nanorods on the wire. The rods were detached from the wire through sonication before observing under TEM. The nanorods can be seen having various sizes. From the single nanorods it could be seen the length is longer than 200 nm and the diameter less than 100 nm. This method of homogeneous nucleation of ZnO might have caused the nonunifrom growth of ZnO nanorods [12].

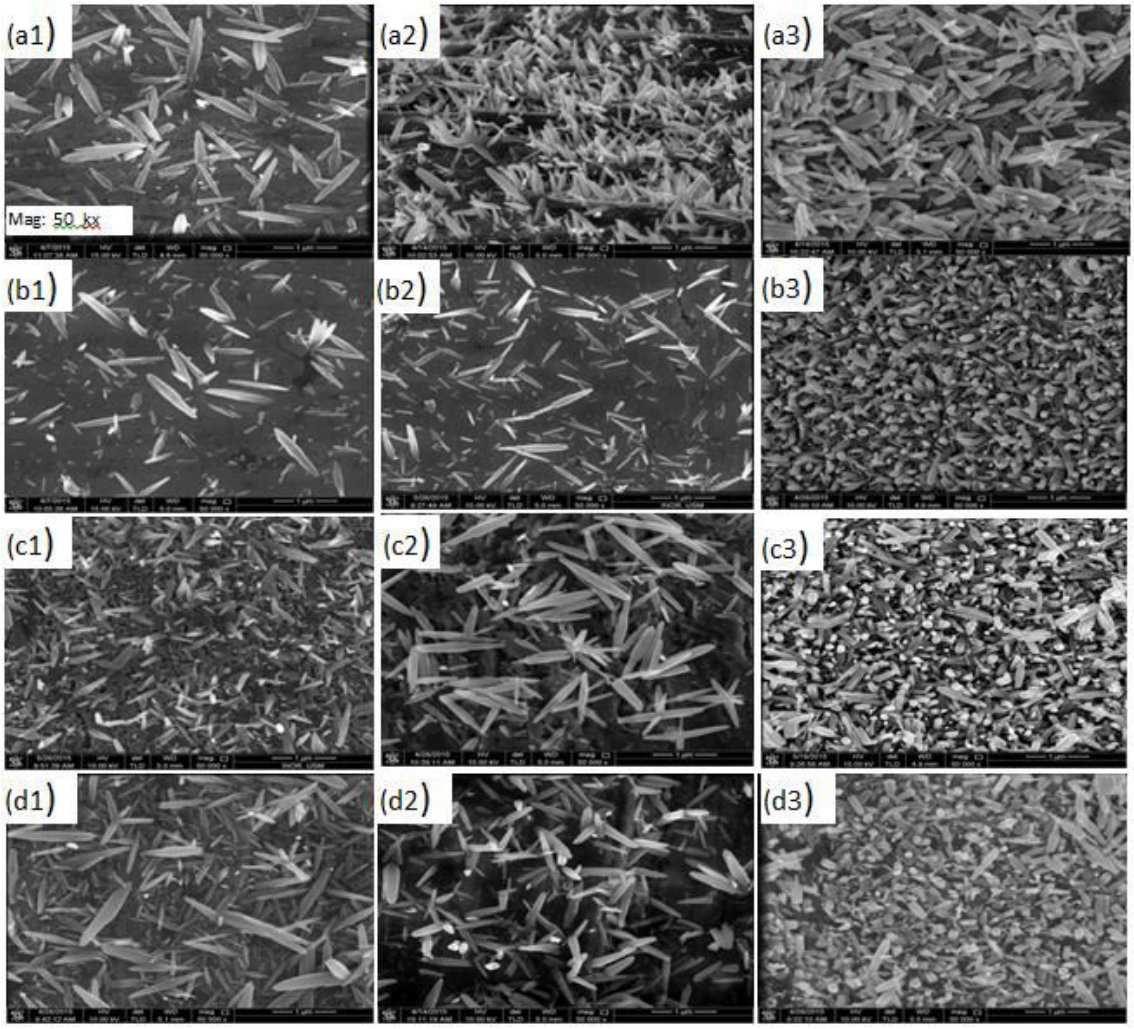

Figure 2: SEM images of ZnO nanorods grown on Ag, Ni, Cu and W wire at different concentrations Figure a, b, c, and d represent wires Ag, Ni, Cu and W. Label 1, 2, and 3 represent the concentrations 0.005 M, 0.01 M, and 0.05 M. The trend shows the increase in density of nanorods grown on wire with increase of precursor concentration.

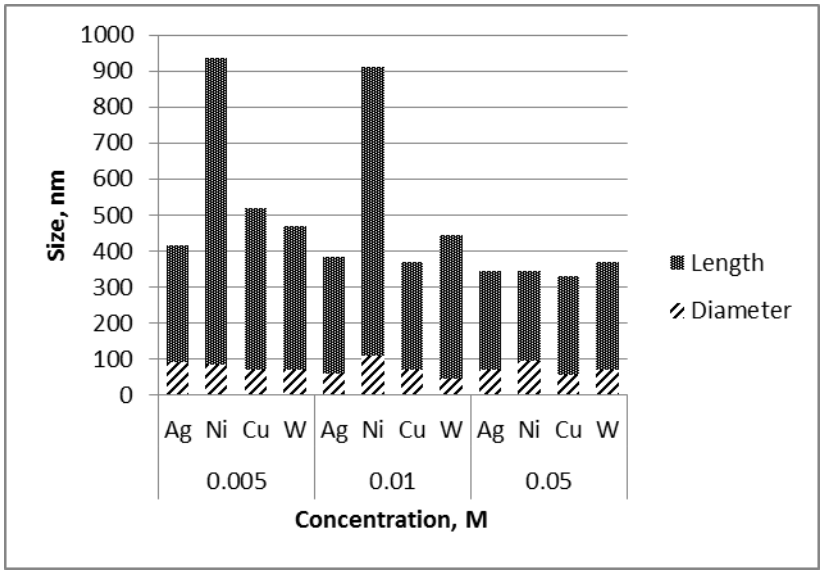

Figure 3: Average length and diameter of ZnO nanorods

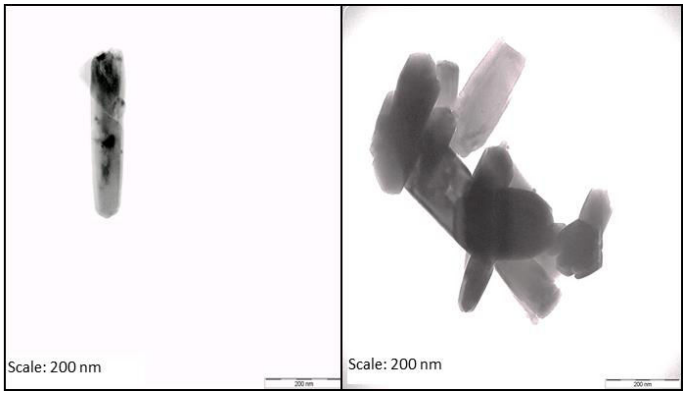

Figure 4: TEM image of ZnO nanorods

In this work, HMT undergoes decomposition by sonication and OH^- ions are formed. Successively during the crystal growth phase, the ZnO nuclei are formed. Therefore HMT plays a crucial role in growth of ZnO nanorods as it supplies OH ions which are a key role in formation of ZnO nanorods [13]. For ZnO nanorods grown on Ag wire at 0.05 M it could be observed that some nanorods had formed bipods instead of single crystalline rods. It could be assume that there might be an extra stage in the growth process which is the linkage stage apart from nucleation and crystal growth stage. The nanorods are seen fused to form single crystalline bipods [8].

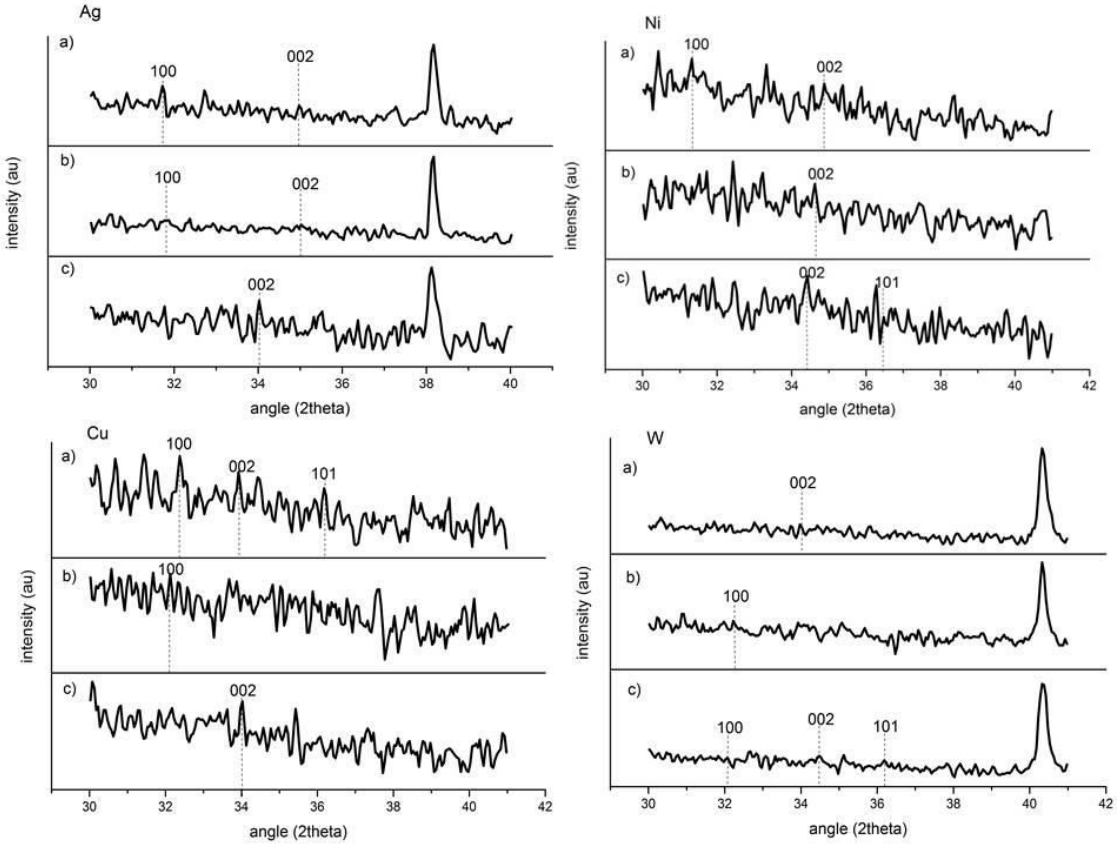

Figure 5: XRD diffraction patterns of ZnO nanorods grown on metal wires at different concentrations 0.005 M, b) 0.01 M, c) 0.05 M

Table 1: Peaks of ZnO

Wire type/ Concentration (M)	0.005 M	0.01 M	0.05 M
Ag	31.674° 34.925°	31.875° 34.936°	34.082°
Ni	31.425° 34.984°	33.937°	34.612° 36.826°
Cu	32.075° 34.184° 36.243°	32.032°	33.973°
W	34.631°	32.228°	32.025° 34.525° 36.122°

XRD was performed after the growth of nanorods on the wires. The X-ray spectrum in Figure 5 shows the peaks of the ZnO and the metal wires. There were some limitations while performing this characterization. There might have been low count of ZnO nanorods present on the wires. Therefore, the X-ray beam could only detect the metal

wires, giving only an intense and sharp peak of the metal wire which is observed for all four Ag, Ni, Cu and W wire. The exact peak values of ZnO are shown in Table 1. However the graph shows only a small, slightly broad peak of ZnO. Overall, ZnO has around 4 to 5 peak for all the samples. They are 31°, 34.5°, 56°, 66°, 70°, and 75°. Although the samples of ZnO at different concentrations have a few different peaks, within 30°-40°, it could be seen in Figure 5 and Table 1 that most of the samples have constant peak at around 34° for ZnO. However ZnO nanorods grown on Cu and W wire at concentration 0.01 M only has peak at 31°. The rest of the samples at concentrations 0.005, 0.01 and 0.05 M showed the peak at around 34.5°. The most prominent peak for ZnO is around 31°, 34° and 36°. However at the lowest concentration, there is a slight deviation of the peak when compared to the database. For Ag wire at 0.005 M and 0.01 M, there is a diffraction peak of 100 and 002 while at 0.05 M, only 002 peak. For Ni wire, there is a diffraction peak of 100 and 002 at 0.005 M, at 0.01 M there is only 002 peak while at 0.05 M the diffraction peak is at 002 and 101. For Cu wire there is a diffraction peak of 100, 002 and 101 at 0.005 M, peak 100 at 0.01 M and peak 002 at 0.05 M. For W wire diffraction peak is observed at only 002 for 0.005 M, peak of 100 at 0.01 M and all three 100, 002 and 101 peak at 0.05 M.

Figure 6 shows the diffraction pattern of ZnO grown on Cu plate. Since the diffraction pattern was poor on the 0.25 µm metal wires, the exact experimental condition as before was maintained and precursor concentration of 0.05 M to grow ZnO nanorods had been applied to observe the growth pattern on a much larger metal plate which in this case is copper. A clear and sharp peak of ZnO are observed at 31.9°, 34.5° and 36.3° which depicts diffraction plane of 100, 002 and 101. Peak at ≈ 34.5° indicated the growth of ZnO nanorods is preferential toward the c-axis in the 002 direction. This is considered to be the most favorable plane for the wurtzite structure [1]. No other diffraction peaks are observed other than ZnO and Cu showing that the sample is pure. The peaks of Cu are above 40°. The larger size of the metal plate provides larger surface area for growth of ZnO nanorods to occur. With increased amount of ZnO present, this proves to be the reason for obtaining a more visible peak of ZnO. It is assumed that ZnO are also present on the 100 µm wires even though the result does not show visible peaks due to low count of ZnO.

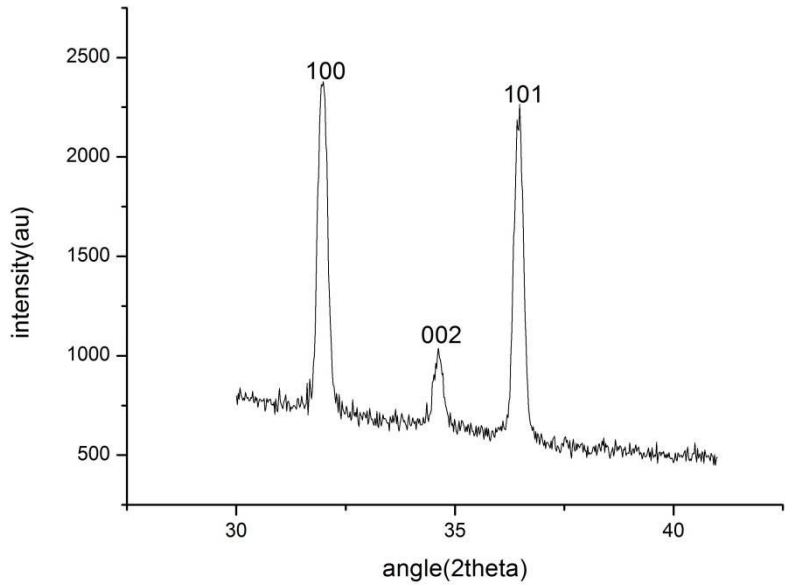

Figure 6: XRD diffraction pattern of ZnO on Cu plate

CONCLUSION

In conclusion, this paper described the properties of ZnO nanorods grown directly on wire using sonochemical method. A fast and efficient method for growth of ZnO nanorods was established in this work. By only using a simple one system method using ultrasonic processor, we were able to grow nanorods on metal wires. The successfully grown ZnO nanorods on wire should then be tested for biosensing applications in future work to be used as high performance electrode. Further research should be done to improve the quality of ZnO nanorods so that it could be exploited for large scale industrial applications.

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