Effect of Flow Rate on Characterizations of ZnO Nanofibers using Electrospinning Method

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الخـــلاصـــــة

تم تحضيرالياف نانوية من اوكسيد الزنك بتركيب متعدد التبلور باستخدام تقنية الغزل الكهربائي.لقد أظهرت قياسات حيود الاشعة السينية ان الالياف النانوية لاوكسيد الزنك تمتلك تركيب سداسي .أن تأثير عامل معدل الانسياب على ألياف أوكسيد الزنك النانوية تم دراسته من خلال أجراء فحوصات المجهر الذري الماسح والمجهر الالكتروني الماسح .تم حساب فجوة الطاقة البصرية وكذلك السلوك البصري باستخدام مطياف الاشعة فوق البنفسجية – المرئية حيث وجد أن فجوة الطاقة البصرية هي (3.9) ألكترون– فولت. كما لوحظ أزدياد معدل قطر الليف النانوي من (٨٢ – ١٣٢) نانومتر بزيادة معدل الانسياب من (١– ٣) مل/ ساعة على التوالي. أن طول الليف النانوي يصل لعدة مايكرونات.

Abstract

ZnO nanofibers with polycrystalline structure were synthesized by an electrospinning method. X-ray diffraction measurements showed that ZnO nanofibers have pure hexagonal wurtzite structure. The effects of flow rate parameter on ZnO nanofibers were examined using atomic force microscopy, field emission scanning electron microscopy. The optical energy gap was estimated and optical behavior was studied using UV-Vis spectroscopy. It was found that the optical energy gap is (3.9) eV. It was noted that the average diameter of these nanofibers increases from (82-132) nm with increasing the flow rate from (1- 3) ml/h respectively. The length of the nanofibers reached to several microns.

Keywords: ZnO, nanofibers, Electrospinning, flow rate.

Introduction

One-dimensional (1D) nanomaterials with high surface to volume ratio have attracted attention because of their exceptional chemical and physical properties and various applications [1-3]. There are many kinds of

1D nanostructures such as nano-belts, nanoneedles, nanorods, nanorings, nanowires, nanotubes, and nanofibers. The nanofibers have many industrial applications used in a variety of fields such as sensors, filtration, biological cells, electronic devices, and protective clothing, etc. [4, 5].

In Comparison with other techniques, electrospinning has advantages of simplicity, low cost, process controllability and capability for producing industrial quantities [6]. Furthermore, electrospinning method has attracted extensive attention in several areas, including photocatalysis, lithium-ion batteries, gas sensor, and dye sensitized solar cells (DSSC) [7-11]. Electrospinning technique has been commonly used to construct different nanostructures (nanotubes, nanobelts, and nanofibers) [12-14].

Electrospinning has been widely used to synthesize nanofibers of oxide materials [15, 16]. In the typical method of electrospinning, high electrical potential is applied between a tip of syringe needle and a target. When the electrostatic force exceeds the surface tension of the liquid droplet formed at the syringe needle tip, charged fluid jet is ejected which is then stretched to form a continuous nanofibers, which are deposited on a target plate [17]. During its flight to a collective target, the ejected, charged jet dries out, leaving ultra thin fibers on the target. The non-woven mat has a high surface area with relatively small pore size [18].

The parameters and processing variables that affect the electrospinning process are: (a) System parameters such as molecular weight (Mw) of the polymer, and polymer solution properties (viscosity, conductivity, and surface tension). (b) Process parameters such as applied electric potential, flow rate and, distance between the syringe needle tip and the target plate. (c) Ambient parameters such as temperature and humidity [19].

Among the 1D transition metal oxides, ZnO has some distinct characteristics such as being non-toxic, having a wide band gap of 3.37 eV at room temperature, having a largely excited binding energy, being inexpensive, and containing photochemical properties. Moreover the 1D Nanosized ZnO is suitable candidate for solar cells, sensors, optoelectronics devices due to its transparent and conductive property [1, 2, 20].

The aims of the current work are to synthesize ZnO nanofibers by electrospinning technique using polyvinylpyrrolidone (PVP) polymer and zinc acetate as precursors. The effect of the flow rate as one of significant processing parameters was then investigated on morphology, and microscopy of electrospun ZnO nanofibers. ZnO nanofibers were characterized by XRD, AFM, FESEM, and UV-Vis, spectroscopy.

Experimental

To fabricate 1D nanostructure ZnO nanofibers, the electrospinning process was adopted. Two separate solutions, one containing zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$, Junsei Chemical) and the other containing

polyvinylpyrrolidone (PVP, M_W: ~1,300,000, Sigma Aldrich) were prepared as precursor solutions. The PVP solution was made by dissolving 1 g of PVP into 10 mL of ethanol (EtOH, 99.9%) and the other solution was made by having 3 g of zinc acetate being added into 10 mL of distilled water. Both solutions were stirred for 5 h at room temperature separately. After this step, 1 mL of the zinc acetate solution was added to the PVP-ethanol solution then this solution was stirred for 4 h. The mixed solution was used as a precursor for electrospinning.

The Zn/PVP solution was loaded to a plastic syringe equipped with a tip of 21-gauge stainless needle. The syringe was placed on a syringe pump (KDS scientific). A high voltage of 20 kV from a Gamma High Voltage Research ES30P power supply was applied to the needle tip. The grounding electrode from the same power supply was attached to a plate of aluminum with clean glass substrates fixed on it which was used as the collector plate and was placed 20 cm in front of the tip of the needle. As soon as an applied voltage is subjected across the needle tip and the collective target plate, a fluid jet was ejected from the needle tip. The feed rate of the precursor solution was (1, 2, and 3) ml/h which can be controlled using a syringe pump. As the fluid jet accelerated to the collector target, the solvent evaporated, leaving only nanofibers on the collector target as shown in figure (1). The obtained nanofibers were left exposed to humidity for approximately 12 h to allow complete hydrolysis and subsequently subjected to calcination at a high temperature of 500 ^{o}C for 3 h with a heating rate of 5^{o}C/min to remove residual PVP polymer.

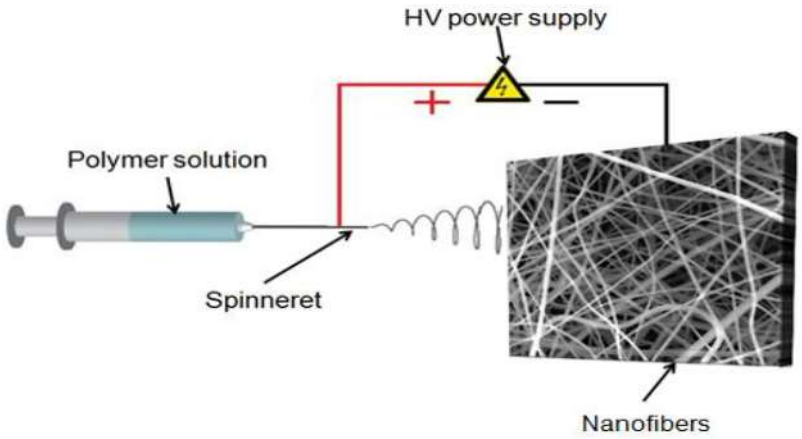

Figure (1): Schematic view of electrospinning technique.

The X-ray diffraction (XRD) measurements, which were used to characterize the crystalline phase of the ZnO nanofibers, were carried out on an X-ray diffractometer (type miniflex II Rigaku, Japan) using (CuKα) radiation. Atomic force microscopy (AFM) micrographs were taken with a Digital Instruments, (Inc. Nanoscope III and Dimension 3100). The

samples were detected under a (Hitachi S-4160 Japan) field emission scanning electron microscope (FESEM). The optical absorption spectra of the ZnO film were verified using (Optima Sp-3000 plus UV-Vis-NIR, Split- beam Optics) spectrophotometer with a wavelength range of (200-900) nm.

Results and discussion

Figure (2) shows the XRD patterns of the as-prepared samples calcined at 500 ^{o}C for 3 hours in air atmosphere. The peaks shown in the XRD patterns correspond to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes. All apparent diffraction peaks confirmed the formation of the pure hexagonal wurtzite structure of ZnO nanofibers with high crystallinity [21]. No other diffraction peaks were detected, which indicates that there were no impurities present and the precursors had been completely transformed into ZnO. It was observed that different flow rates gives the same XRD spectrum.

The surface morphology and roughness have been indicated in figure (3) using AFM images, the roughness average is (2.17, 1.14, and 0.154) nm for the fibers prepared in (1, 2, 3) ml/h respectively. The roughness average increased with the flow rate decreased, and this has great advantages in many applications of ZnO nanofibers such as sensing and photocatalyst applications. The grain size average values were (74.08, 82.02, and 89.66) nm for the fibers prepared in (1, 2, 3) ml/h respectively. This means that the average grain size decrease with decreasing the flow rate. Figures (4) shows diameter size distribution of ZnO nanofibers prepared in different flow rates. All these figures take the favorite Gaussian distribution.

ZnO nanofibers were investigated by FESEM analyses as shown in figure (5). The distributions of the nanofibers are continuous and fairly random. The average diameter are (82, 120, and 132) nm for ZnO nanofibers prepared in (1, 2, 3) ml/h respectively. This indicates that the slower flow rate is better to obtain the smaller fiber diameter. The length of the nanofibers reached to several microns, therefore they have a very high aspect ratio.

Figure (6a) shows the variation of the transmittance with the flow rate, the transmittance decreases with increases the flow rate, while the optical energy gap remains unchanged and equal to (3.9 eV) as it shown in figure (6b) .This relatively large value of optical band gap is usually observed when we are dealing with the nanoscale, therefore this blue shift of the band gap was taken place because of the quantum confinement effect [22, 23].

Conclusions

Nanofibers of ZnO have been successfully fabricated using an electrospinning method. This method is simple and repeatable. ZnO

nanofibers (diameter of ~82–132) nm could be obtained and confirmed by XRD and the crystalline phase in the form of pure hexagonal wurtzite structure. The flow rate is an important parameter in the electrospinning technique, and the effect of this parameter was considered on average diameters, roughness, and energy gap of ZnO nanofibers. Since the average diameter of ZnO nanofibers is much smaller than the length of the fiber, therefore very high aspect ratio is obtained.

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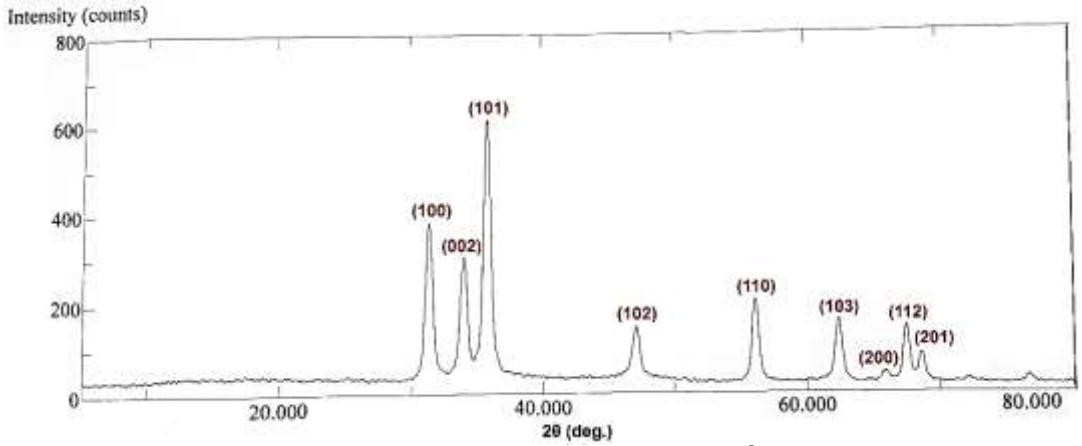

Figure (2): XRD spectrum of ZnO

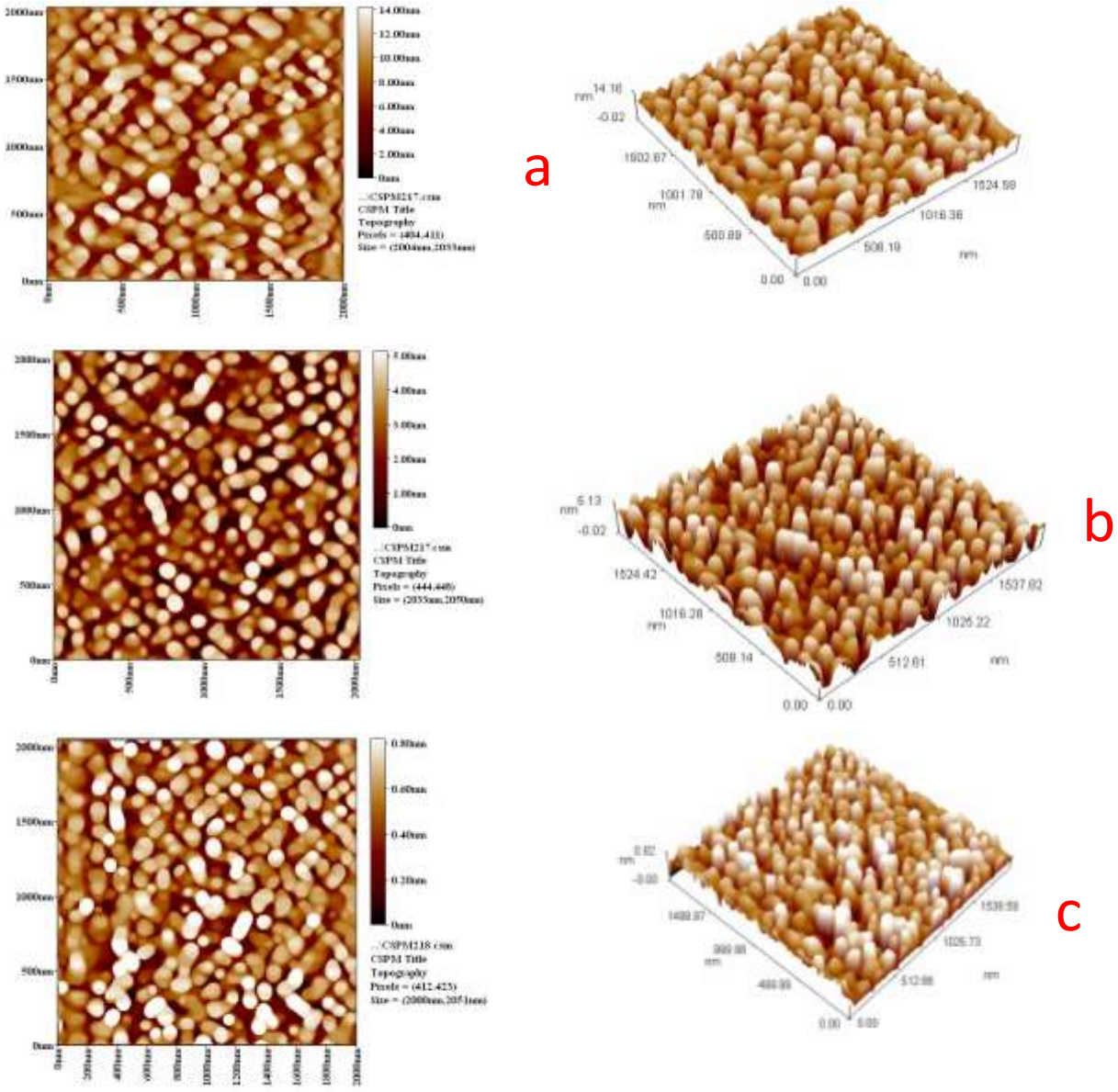

Figure (3): AFM micrographs of ZnO nanofibers prepared in different flow rates (a) 1 ml/h (b) 2 ml/h (c) 3 ml/h.

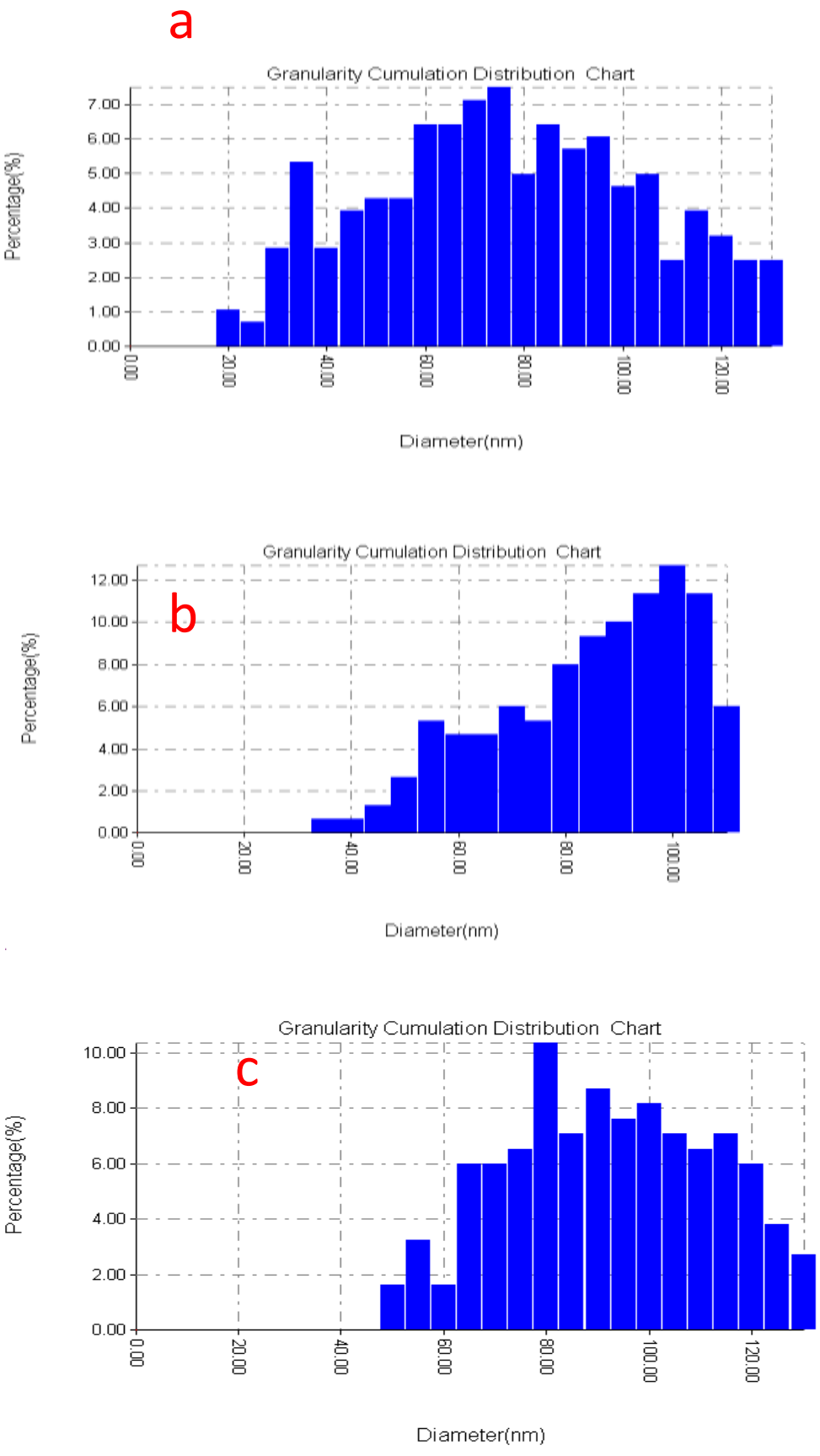

Figure (4): Diameters size distribution of ZnO nanofibers prepared in different flow rates (a) 1 ml/h (b) 2 ml/h (c) 3 ml/h.

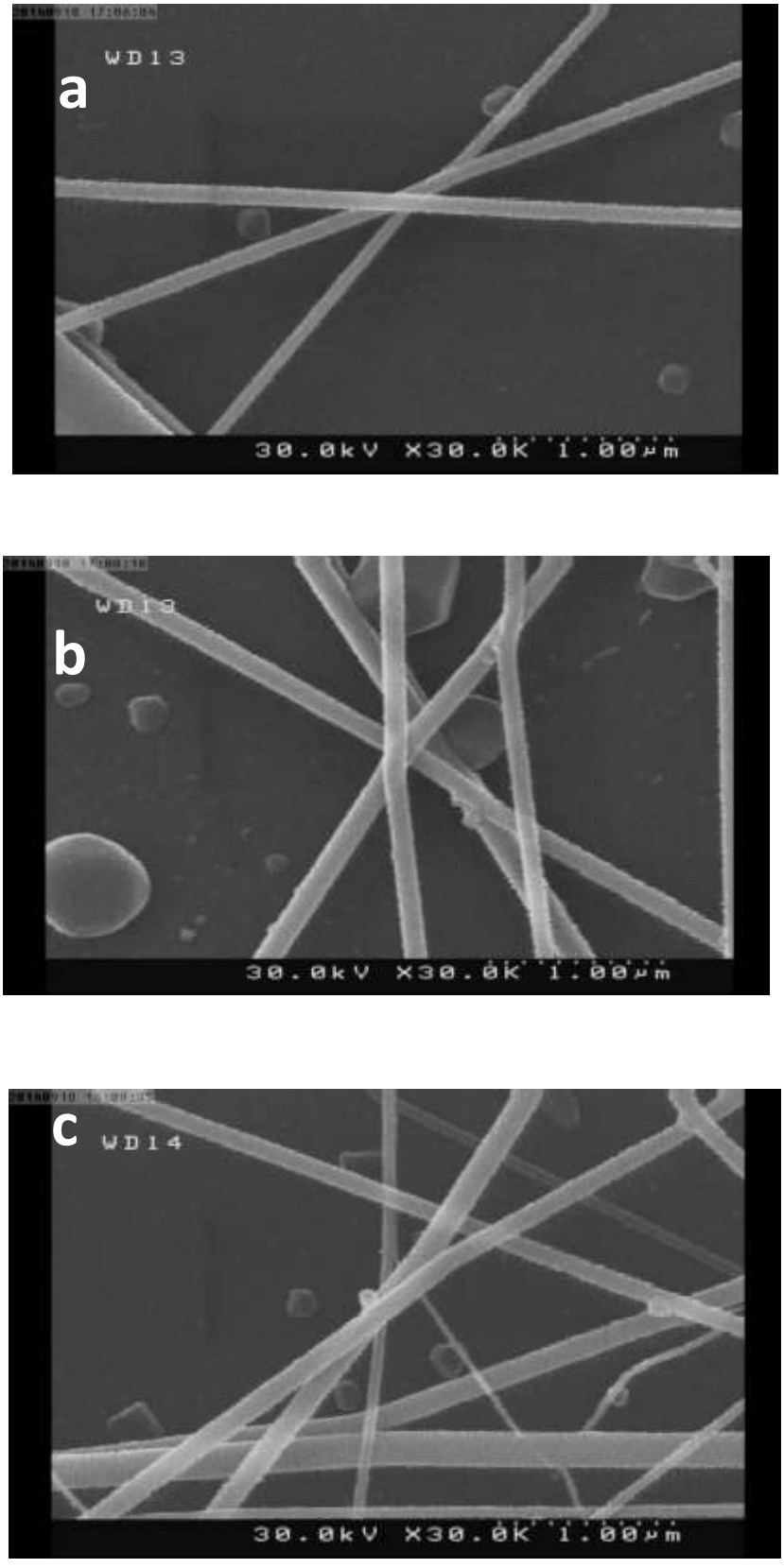

Figure (5): FESEM images of ZnO nanofibers prepared in different flow rates (a) 1 ml/h (b) 2 ml/h (c) 3 ml/h.

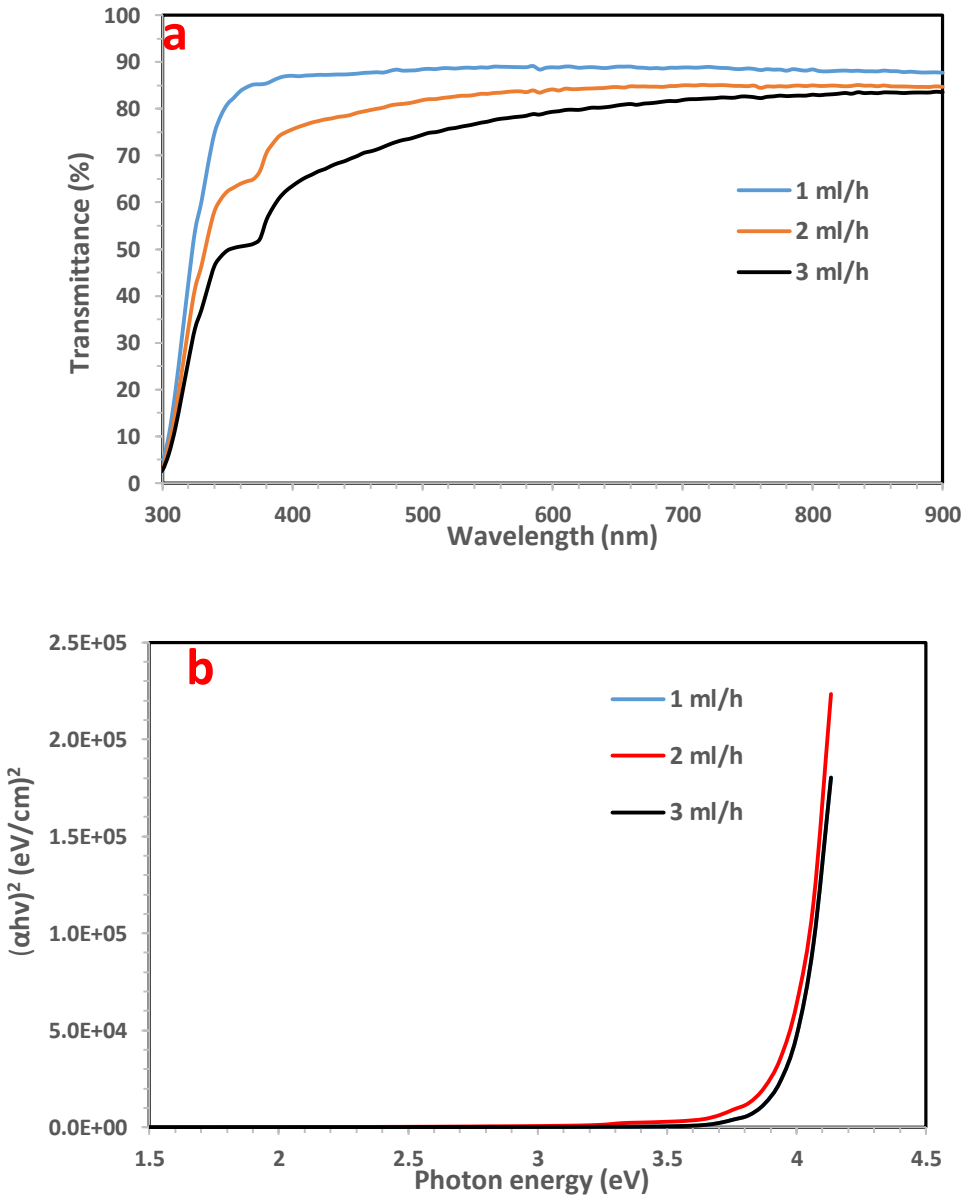

Figure (6): (a) The transmittance vs. wavelength of ZnO nanofibers prepared in different flow rates (b) The allowed direct band gap prepared in different flow rate.