

Fabrication of electro spinning 1D ZnO Nano fibers as UV-Photoconductor

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Abstract

The electrospinning technique was used to fabricate 1D nanofibers of Zinc Oxide (ZnO). Polyvinylpyrrolidone (PVP)/ zinc acetate Nano fibers electrospun using solution containing PVP dissolved in ethanol and zinc acetate in distilled water were mixed, followed by calcination at 500°C for 3 hours to remove the polymer. XRD pattern show the hexagonal wurtzite structure of ZnO NFs without any impurities. FESEM pictures show a network of nanofibers with diameters less than 100 nm and several micrometers in length of ZnO, these nanostructures increase the ratio of surface area to volume and improve the physical properties of the materials. The Photoluminescence (PL) of the films was studied and the energy gap and the optical properties were estimated. A photoconductor device was constructed by electroding the films with silver conducting electrode (IDE) using screen print method, The result shown that the resistance of the nanofiber films decrease dramatically when exposes to UV light. In addition, the change of conductivity with the change of wavelengths was studied also the photoconductivity was examined under different bias voltage.

Keywords: ZnO, nanostructures, electrospinning, photoconductivity.

تكوين اليفانانوية لأوكسيد الزنك الاحادي الاتجاه بأستخدام البرم الكهربائي كموصل ضوئي للأشعة فوق البنفسجية

الخلاصة

تم استخدام تقنية الدوران اللولبي الكهربائي لتحضير اليفانانوية من اوكسيد الخارصين. تم الحصول على الاليفانانوية ل PVP و خلاصات الزنك من خلال ضخ محلول يتكون من PVP مذاب في الايثانول و خلاصات الزنك المذاب في الماء المقطر حيث تم مزجها، يتبعه حرق للغشاء المتكون بدرجة حرارة 500 م° لمدة 3 ساعات للتخلص من البوليمر. يبين نمط ال (XRD) ان اوكسيد الخارصين يكون ذات تركيب سداسي و بدون شوائب. أظهرت صور FESEM شبكة من الاليفانانوية التي تتراوح اقطارها دون ال 100 نانومتر وطولها عدة مايكرومترات. ان هذه التراكيب النانوية تزيد من نسبة المساحة السطحية الى الحجم مما يؤدي الى تحسين الخصائص الفيزيائية للمواد. تم دراسة التألقية الضيائية وكذلك حساب فجوة الطاقة والخصائص البصرية للاغشية المحضرة. تم بناء الموصل الضوئي بعد تقطيب الاغشية ب (IDE) باستخدام طريقة الطباعة على الشبكة وظهرت النتائج انخفاضاً كبيراً في مقاومة الاليفانانوية عند تعرضها للضوء ضمن المنطقة فوق البنفسجية.

بالإضافة الى ذلك تم دراسة تغير التوصيلية مع تغير الطول الموجي وكذلك التوصيلية الضوئية بفولتيات انحياز مختلفة.
الكلمات المرشدة: اوكسيد الخارصين، تراكيب نانوية، الدوران اللولبي الكهربائي، التوصيلية الضوئية.

INTRODUCTION

One-dimensional (1D) nanostructures have been a subject of intensive research due to their unique properties and interesting applications in many areas [1]. It provides a good system to investigate the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction, and play an important role for both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices with nanoscale dimensions [2]. There are many kinds of 1D nanostructure such as nanorods [3], nanoneedles [4], nano-belts, nanorings [5], nanotubes [6], nanowires [7], and nanofibers [8].

1D Zinc oxide (ZnO) has been widely used in the production of optoelectronic devices [9], photocatalysts [10], solar cells [11, 12], gas and chemical sensors [13, 14], detector [15], etc.. It exhibits high efficiency in the UV Photoconductive detector [16] due to its large band gap (~3.37 eV), large exciton binding energy (~60meV), good thermal stability, and large specific surface area [17]. There are several methods for ZnO production, such as sol-gel process [18], electrospinning [19], precipitation in water solution, hydrothermal synthesis, vapor deposition, precipitation from micromulsions and mechanochemical processes, makes it possible to obtain products with particles differing in shape, size, and spatial structure [20].

Among many techniques, which allow obtaining ZnO, electrospinning is one of the most simple, versatile, low-cost, and effective [21]. This method has an attractive potential for producing NFs from Polymers, Composites or Ceramics with diameters ranging from tens of nanometers to microns [22]. Furthermore, nanofibers length and diameter are controlled by solution and processing parameters [23].

The present work reports the synthesis of ZnO nanofibers by electrospinning method, which characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), photoluminescence (PL), UV-visible, and Ultraviolet photoelectric properties.

Experimental part

To produce ZnO Nano fibers, the electrospinning process was adopted. Polyvinylpyrrolidone (PVP) with a molecular weight of (~1,300,000) and zinc acetate $Zn(CH_3CO_2)_2 \cdot 2H_2O$ were used as the precursor materials. The PVP solution was prepared by dissolving 6wt. % of PVP in ethanol, and zinc acetate solution by dissolving 40 wt. % in distilled water. Both solutions were stirred for 1hour at room temperature separately. Then, 7.5 wt. % of zinc acetate solution was transferred to PVP solution with constant stirring for 2hours at room temperature. A viscous mixed solution of zinc acetate plus PVP was obtained.

The mixed solution was loaded into a plastic syringe (5 ml) connected to 21-gauge stainless steel needle. The distance between the tip of syringe needle and Al collector was 20 cm and the feeding rate of the solution was adjusted at a constant rate of 1ml/h. A high voltage of 16 KV was applied to the metal needle tip. The resulting electrospun Nano fibers were then calcined at 500°C for 3 h. Then, the Photoconductor device was constructed by electroding the films with silver

conducting electrode (IDE) using screen print method. The flow diagram of fabricating ZnO Nano fibers photoconductor is shown in fig. (1).

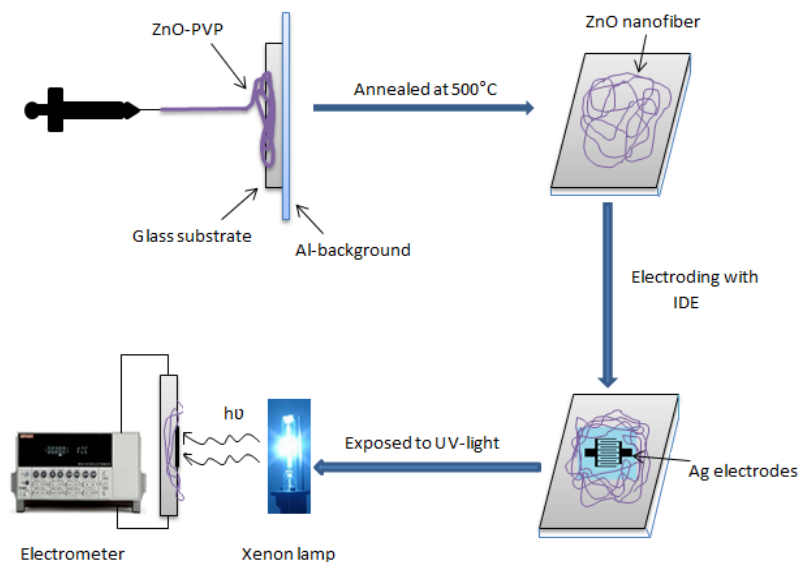


Figure (1) Flow diagram of fabricating ZnO NFs photoconductor.

X-ray diffraction (XRD) of the calcined nanofibers was conducted on a (miniflex II Rigaku, Japan) with Cu α radiation. Field emission scanning electron microscopy (FE-SEM) images were recorded by (Hitachi-S 4160-Japan), while working at (15) kV acceleration voltage. UV- visible measurement of the ZnO NFs recorded by using Optima Sp-3000 plus UV-Vis-NIR (Split- beam Optics, Dual detectors) spectrophotometer. The room temperature Photoluminescence (PL) spectrum was performed on Perkin Elmer Spectrophotometer Luminescence LS 55 equipped with FL Win lab software with a pulsed Xenon discharge lamp as the exciting source at 325 nm. For the photocurrent measurements a Xenon lamp with power density ($6\mu\text{W}/\text{cm}^2$) was used as the light source. For current–voltage measurement, Keithly-2430 digital electrometer, a dual Farnel LT30/2 -3 to 3V power supply were used.

Results and discussions

The XRD patterns of the ZnO NFs are shown in fig. (2). Several well-defined diffraction reflects characteristic of ZnO NFs were observed in the obtained XRD pattern. These reflections appeared at 31.36° , 34.02° , 35.86° , 47.14° , 56.16° , 62.46° , 67.54° and 68.68° correspond to the lattice planes of (100), (002), (101), (102), (110), (103), (112) and (201), respectively. This peaks can be indexed to the hexagonal wurtzite structure of ZnO ($a=3.249 \text{ \AA}$, $c=5.206 \text{ \AA}$, JCPDS 36-1451). No other diffraction peaks were detected, which indicates that there were no impurities present and the precursors had been completely transformed into ZnO.

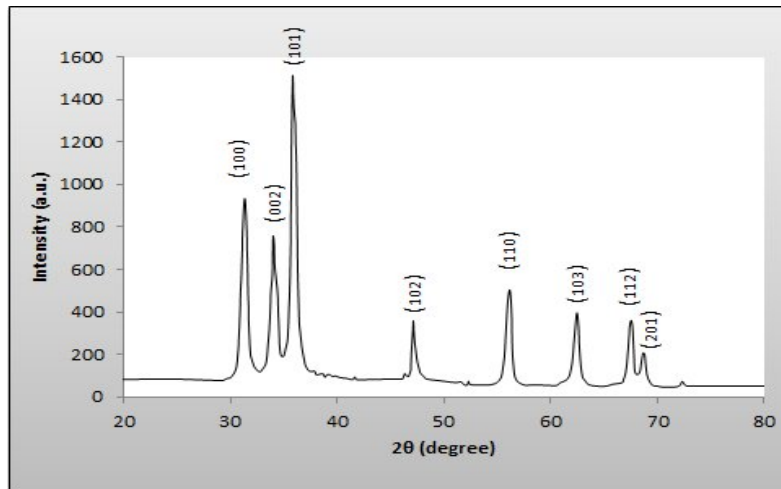


Figure (2) XRD pattern of ZnO NFs .

Field emission scanning electron microscope (FE-SEM) images of zinc oxide - PVP composite nanofibers and ZnO nanofibers are shown in fig. 3 (a) and (b), respectively. As observed, the length of the fibers can even reach the micrometer range. In both cases, the distributions of the nanofibers are continuous and fairly random. Fig. (3a) showed that the surface of the composite zinc oxide - PVP are smooth and have an average diameter (90 - 200) nm. As shown in fig. (3b), the diameter of ZnO nanofibers after calcination process, are decrease to (~40) nm. This size reduction of the fibers is due to the removal of the PVP during the calcination process and the crystallization of ZnO.

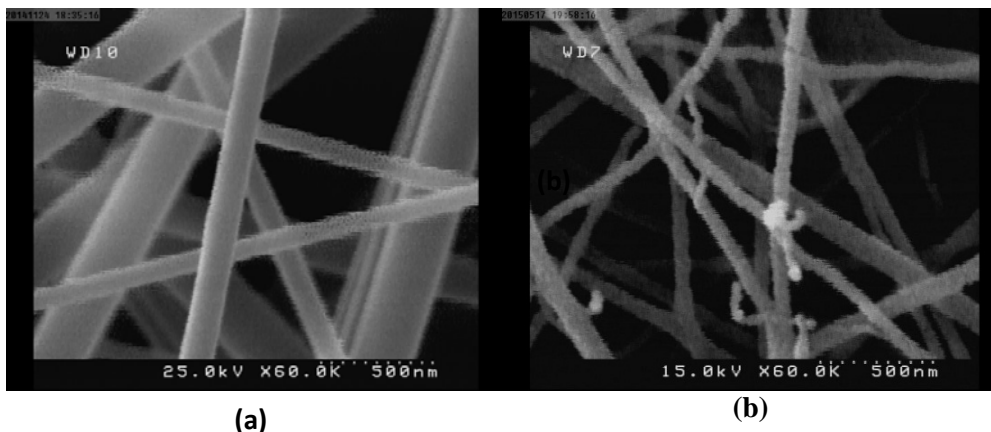


Figure (3) FE-SEM images of: (a) Zinc acetate / PVP composite, and (b) ZnO after calcination at 500°C.

The optical properties of the ZnO NFs in the wavelength range of 340 to 900 nm were investigated through UV- visible spectroscopy at room temperature and shown in fig. (4). The absorption spectra show that the absorption edge of the ZnO NFs is

around 360 nm, indicating that the ZnO NFs have the characteristic of UV light preferred absorption as shown in fig. (4a). The typical room temperature transmittance spectra for ZnO NFs are shown in fig. (4b). The transmission spectra of the ZnO NFs show just opposite trend of the optical absorption spectra. The optical band gap (E_g) was determined by tauc relation [24, 25]:

$$\alpha h\nu = A (h\nu - E_g)^n \dots (1)$$

Where A is constant, $h\nu$ is the incident photon energy, α is the optical absorption coefficient near the fundamental absorption edge, E_g is the energy band gap and $n=1/2$ for direct band gap. The energy band gap of the ZnO NFs can be obtained by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portion of the absorption edge with the energy axis as shown in fig. (4c). the band gap of ZnO NFs is (3.4 eV) and this shift tendency related to the confinement of the 1D ZnO nanostructure.

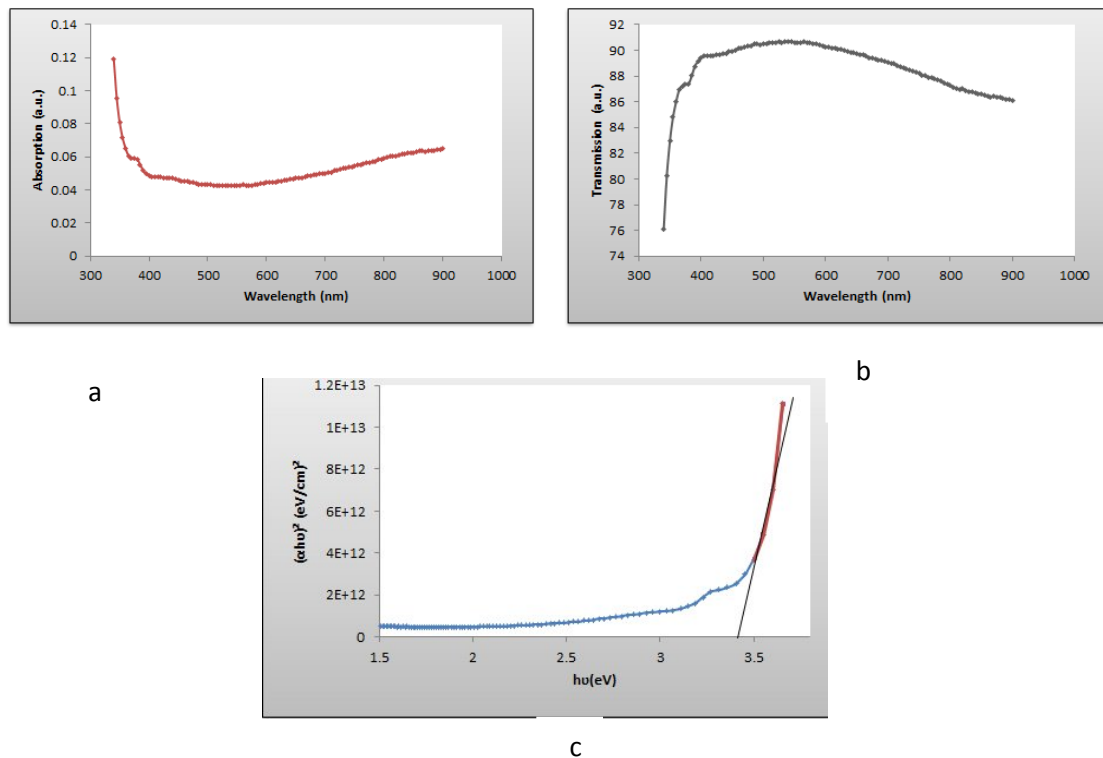


Figure (4) (a) Absorption spectra, (b) transmittance spectra, and (c) optical band gap of ZnO NFs.

Photoluminescence (PL) spectra of the ZnO NFs were obtained at room temperature is shown in fig. (5). The PL spectra demonstrated two dominant peaks, which had UV emission at 381 nm and visible emission around 484 nm. The first

emission band that was located in the UV range was related to the recombinations of free excitons. In addition, the second emission band is a broad green luminescence emission peak is generated by various point defects such as oxygen vacancies, zinc vacancies, oxygen interstitials and zinc interstitials [26].

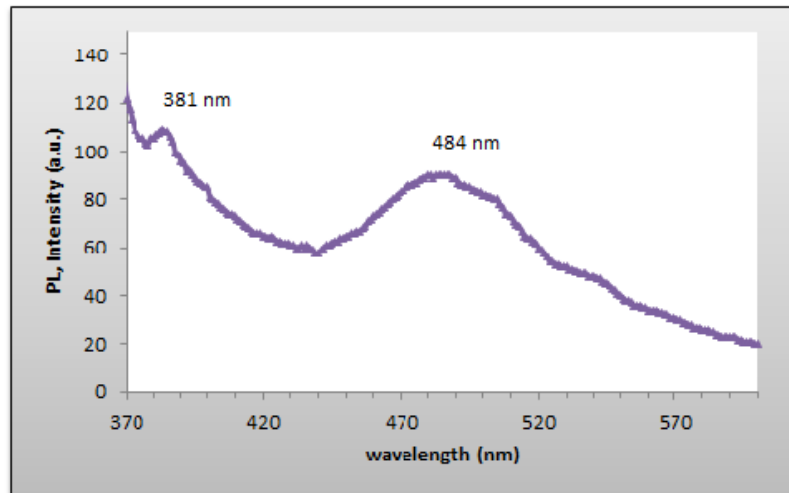


Figure (5) photoluminescence spectra of ZnO NFs at glass substrate.

Surface area plays a very important role in the UV mechanism, as the sensing mechanism involves the surface reactions between the free carriers and Oxygen molecules in environment. The nanofiber area possesses a high surface area on the film surface that is suitable for UV photoconductive sensor applications. In general, the photo-response of a UV photoconductive sensor is influenced by the adsorption and desorption of Oxygen on its surface under UV illumination. Oxygen molecules were adsorbed onto the nanofiber surface by capturing free electrons from ZnO NFs:



Where O_2 is an Oxygen molecule, e^- is a free electron, and O_2^- is adsorbed Oxygen on the nanofiber surface. When ZnO NFs was exposed to (370 nm) UV light, electron-hole pairs are photo-generated according to the following equation:



Where $h\nu$ is the photon energy, h^+ is a photogenerated hole, and e^- is a photogenerated electron. Then, large surface area availability in the nanofiber film as clear in FESEM result extend a fast surface reaction between photogenerated holes and adsorbed Oxygen:



This process leaves behind the photogenerated electron, which decreases the resistance of the ZnO NFs. When the UV light is turned off, the Oxygen molecule recombines with the electron, which leads to resistance increases back within 10% of

the initial value as shown in fig. (6). The sensor showed relatively fast response and recovery for UV detection.

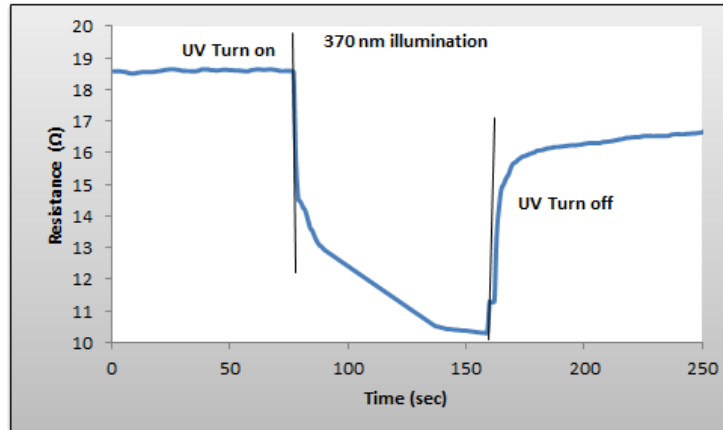
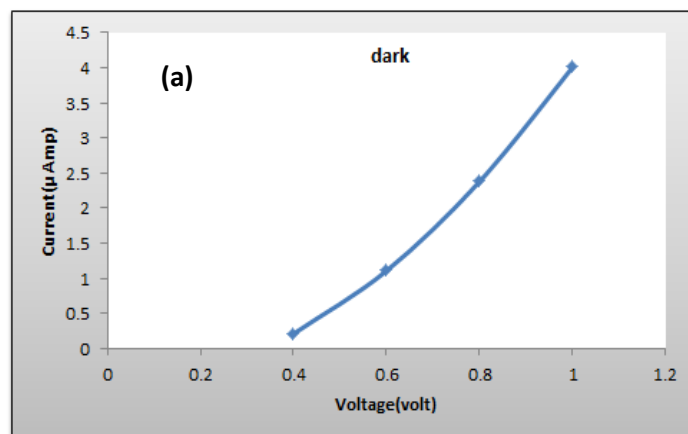


Figure (6) photo response of ZnO NFs fabricated by electro spinning method.

The dependence of current on the applied bias in dark and under UV illumination is shown in fig. 7 (a) and (b), respectively. The current – voltage curve in dark is linear, which indicates Ohmic behavior of the ZnO NFs / Ag contacts. Also, due to the Ohmic nature of contacts in the fabricated photoconductor, the current is expected to be uniform and linear within the range of applied bias. Therefore, the increase in current with applied bias can be attributed to an increase in the consequent reduction of the charge passage time, and carrier drift velocity. Fig. 7 (c) shows the current response of ZnO NFs photoconductor under different UV illumination and at different bias voltages. The device show high spectral selectivity, where the high spectral response for the device is at 370 nm. Also the photocurrent of ZnO NFs device gets higher with the increasing in bias voltage.



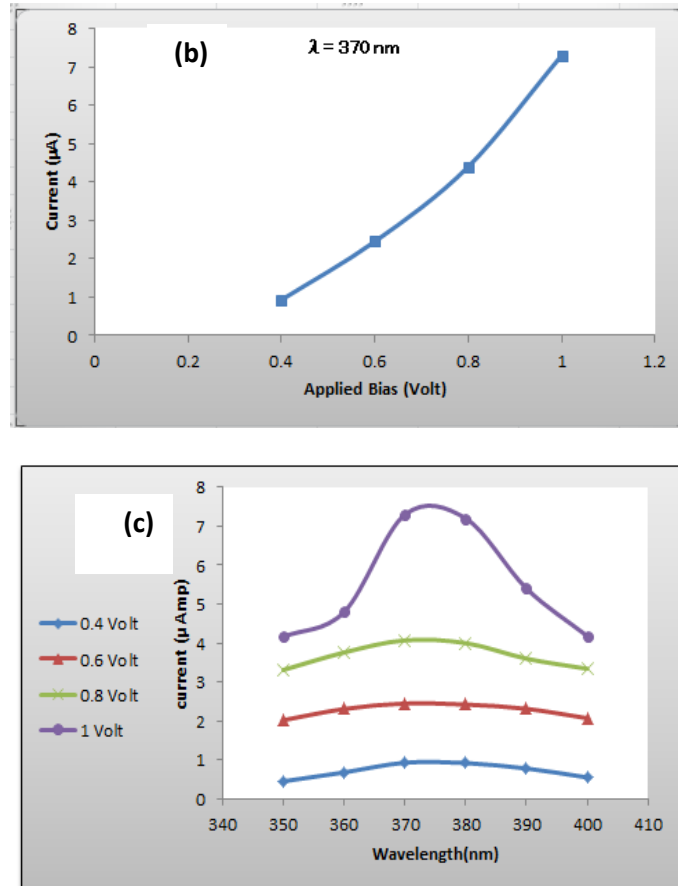


Figure (7) (a) Current – Voltage characteristic of the ZnO NFs in the dark (without illumination), (b) Current – Voltage characteristic of the ZnO NFs under UV illumination (370nm), and (c) photocurrent spectra of ZnO NFs under different wavelength and applied voltage.

Fig. (8) Shows the spectral response characteristic of fabricated ZnO NFs photoconductor with Ag IDE electrodes, were measured at applied bias of 1 Volt. Sharp cutoff occurred at 370 nm for ZnO NFs device. The responsivity of the fabricated ZnO NFs photoconductor under illumination of 370 nm is 3.29 A/W.

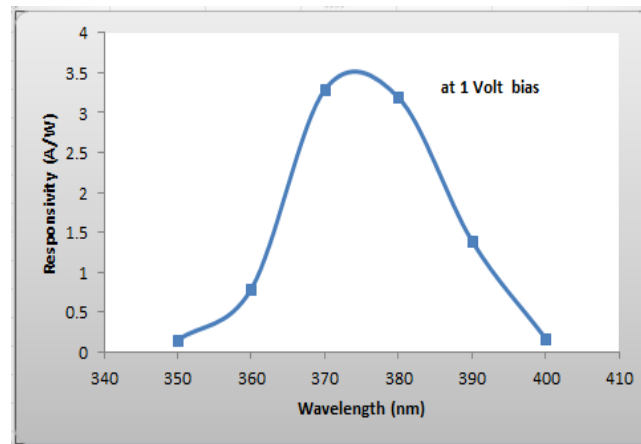


Figure (8) Spectral responsivity of ZnO NFs photosensor at 1 Volt applied bias.

Conclusion:

In summary, fabrication of 1D ZnO nanofibers UV photoconductor by electrospinning technique is demonstrated. When using the ZnO NFs as light absorb layer, the UV light based on ZnO nanostructure obtains excellent photoconductivity and selectivity. The current – voltage characteristic of the photoconductor is very sensitive to UV illumination, which indicates ohmic behavior of ZnO NFs. The large photoresponse of 3.29 A/W is found under the illumination of 370 nm at 1 Volt bias. Also, the photocurrent of ZnO NFs device gets higher with the increasing in bias voltage. This result indicates that the process used is very useful in fabricating high-performance ZnO NFs as UV photoconductor.

References

- [1] Xia Y., Li D., (Electrospinning of Nanofibers: Reinventing the wheel?), *Advanced materials*, Vol. 16, No. 14, p 1151-1170, 2004.
- [2] Xia Y., Sun Y., Yang P., Wu Y., Mayers B., Gates B., Yin Y., Kim F., Yan H., (One – Dimensional Nanostructures: synthesis, characterization, and applications), *Advanced materials*, Vol. 15, No.5, p 353-389, 2003.
- [3] Wang L. Z., (Zinc oxide nanostructures: growth, properties and applications), *Journal of physics: condensed matter*, Vol. 16, p 829-858, 2004.
- [4] Wahab R., Ansari S. G., Kim Y. S., Seo H. K., Shin H. S., (Room temperature synthesis of needle – shaped ZnO nanorods via sonochemical method), *Appl. Surf. Science*, Vol. 253, p 7622-7626, 2007.
- [5] Mende L. S., Macmanus D., (ZnO – nanostructures, defects, and devices), *Materials today*, Vol. 10, No. 5, p 40-48, 2007.
- [6] Chae K. W., Kim J. S., Zhang Q., Jeong Y. H., Cao G., (Low – temperature solution growth of ZnO nanotube arrays), *Beilstein journal of nanotechnology*, Vol. 1, p 128-134, 2010.

- [7] Yang P., Mao S., Yan H., Russo R., Johnson J., Saykally R., Morris N., Pham J., He R., Choi H. J., (Controlled growth of ZnO Nanowires and their optical properties), *Advanced functional materials*, Vol. 12, No. 5, p 323-331, 2002.
- [8] Kang J., Baek J., Park J., Kim D., Wikoh S., Kang Y. C., (Fabrication and thermal oxidation of ZnO Nanofibers prepared via electrospinning technique), *Bull. Korean chem*, Vol. 33, No. 8, p 2694-2698, 2012.
- [9] Chang S. H., Cao H., Xu J. K., Zhang D. Z., Ho S. T., Seeling E. W., Liu X., Chang R. P. H., (Spatial confinement of laser light in active Random Media), *Phys. Rev*, Vol. 84, No. 24, p 5584-5587, 2000.
- [10] Li S. J., Yumoto H., Inoue T., Sako T., Nishiyama K., (Application of ITO films to photocatalysis), *Thin solid films*, Vol. 345, No. 1, p 38-41, 1999.
- [11] Leschkies K. S., Basit J., Divakar R., Pommer E. E., Boercker J. E., Carter C. B., Kortshagen U. R., Norris D. J., Aydil E. S., (Photosensitization of ZnO Nanowires with CdSe Quantum Dots for photovoltaic Devices), *Nano letters*, Vol. 7, No. 6, p 1793-1798, 2007.
- [12] Martinson A. B. F., Hupp J. T., Elam J. W., Pellin M. J., (ZnO Nanotube Based Dye – sensitized solar cells), *Nano letters*, Vol. 7, No. 8, p 2183-2187, 2007.
- [13] Foo K.L., Kashif M., Hashim U., Ali M., (Fabrication and characterization of ZnO thin films by sol- gel spin coating method for the determination of Phosphate buffer Saline concentration), *Current Nanoscience*, Vol. 9, p 288-292, 2013.
- [14] Kashif M., Ali M., Ali S. M. U., Foo K. L., Hashim U., Willander M., (Sol – gel synthesis of ZnO nanorods for ultrasensitive detection of acetone), *Advanced science letters*, Vol. 1, No. 12, p 3560-3563, 2014.
- [15] Chai G., Lupan O., Chow L., Heinrich H., (Crossed Zinc Oxide nanorods for ultraviolet radiation detection), *Sensors and actuators A: physical*, Vol. 150, p 184-187, 2009.
- [16] Hong D., Xiao W., Xiang L., Fang C., Ling W., Yun-Ze L., Yi-Chen L., (Ce – doped ZnO based fast Response UV photoconductive Detector), *Advanced Materials Research*, Vol. 1088, p 377-380, 2015.
- [17] Wei A., Sun X. W., Xu C. X., Dong Z. L., Yang Y., Tan S. T., Haung W., (Growth mechanism of tubular ZnO formed in aqueous solution), *IOP science*, Vol. 17, p 1740-1744, 2006.
- [18] Prakash G. S., (Synthesis and characterization of Zinc Oxide nanoparticles by sol – gel process), *National institute of technology, Rourkela*, 2012.
- [19] Wu H., Pan W., (Preparation of Zinc Oxide Nanofibers by electrospinning), *The American ceramic society*, Vol. 89, No. 2, p 699-701, 2006.
- [20] Agnieszka K., Teofil J., (Zinc Oxide – from synthesis to application: A Review), *Materials*, Vol. 7, p 2833-2881, 2014.
- [21] Anna B., Anna R., Kamil S., Bozena S., Piotr D., Marta A., Lukasz K., Wojciech P., Bogdan J., Tomasz A., Maciej S., Danek E., Krzysztof F., (Magnetic Fe doped ZnO nanofibers obtained by electrospinning), *sol – gel science technology*, 2011.
- [22] Zhang Y. Z., Kotaki M., Huang Z. M., Ramakrishna S., (A review on polymer nanofibers by electrospinning and their applications in nanocomposites), *Composites science and technology*, Vol. 63, p 2223-2253, 2003.
- [23] Wang C., Li Z., (Effects of working parameters on electrospinning), *Springer brief in Materials*, 2013.
- [24] Chandrasekaran G., Elilarassi R., (Structural, optical and magnetic characterization of Cu – doped ZnO nanoparticles synthesized using solid state reaction method), *Mater Electron*, Vol. 21, p 1168-1173, 2010.

- [25] Amornpitoksuk P., Haidoux A., Suwanboon S., Tedenac J. C., (Structural and optical properties of undoped and aluminium doped Zinc Oxide nanoparticles via [26] precipitation method at low temperature), Journal of Alloys and compounds, Vol. 462, p 335-339, 2008.
- [27] Djuricic A. B., Liu Z. T., Li D., Leung H., Xie M. H., Shi S. L., Xu S. J., (Different origins of visible luminescence in ZnO nanostructures fabricated by the chemical and evaporation method), Applied physics letters, Vol. 85, No. 9, 2004.