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Preparation N/M Polycrystalline ZnO Particles for Biosensor Platform Applications

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ABSTRACT

This work reports the syntheses of preparation nano/micro size zinc oxide with polyanaline. ZnO particles were synthesized by simple and efficient method in aqueous media from zinc nitrate without any requirement of calcinations step at high temperature. These particles were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared analysis (FTIR), X-Ray Florescence (XRF), optical transmittance microscope (OTM). The particles distribution size (PDZ)) of powder are calculated. Optical properties of ZnO films by uv-visible and PL spectra for PANi, ZnO/PANi were studied also. This review highlights the potential use of ZnO in modified biosensing applications.

Keywords: Zno Nano/Micro Structures, Chemical Bath Deposition Growth of Zno Powder, Biosensors.

تحضير دقائق ZnO متعدد التبلور لتطبيقات المحتسات البايولوجية

الخلاصة

يتناول هذا البحث مسار تحضير اوكسيد الزنك مع البولي انيلين في المديات(مايكرو/ نانو) . حضرت الدقائق بطريقة المحلول البسيطة والكفؤة في وسط من محلول لنترات الزنك دون اي متطلبات لدرجات حرارة عالية. شخصت هذه الدقائق باستخدام حيود الاشعة السينية XRD وتقنية الـFTIR و XRF والمجهر البصري النافذ . تم قياس توزيع حجوم الدقائق باستخدام تقنية PDZ . الخصائص البصرية درست باستخدام طيف الامتصاص في المنطقة فوق البنفسيجية والمرئية وايضا طيف PL لاغشية من اوكسيد الزنك واوكسيد الزنك مع البولي انيلين. هذه الدراسة هي تسلط الضوء على خصا ئص اوكسيد الزنك لاستخدامه في تطبيقات التحسس البايولوجي .

INTRODUCTION

Nano/Micro structure zince oxide (ZnO) has received considerable attention because of its unique optical, semi conducting, piezoelectric, and magnetic properties, this properties could provide a suitable microenvironment for immobilization of enzymes while retaining their biological activity, and thus lead to an expanded use of this nonmaterial for the construction of electrochemical biosensors with enhanced analytical performance[1].

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A biosensor is an analytical device, which converts the modification of the physical or chemical properties of a biomatrix (e.g., enzyme, antibodies, receptors, organelles, microorganisms) into electric or other kinds of whose amplitude depends on the concentration of defined analytics in the solution. They are becoming essential in the field of healthcare, chemical and biological analysis, environmental monitoring, and food processing industrial. [1]. According to the receptor type, biosensors can be classified as enzymatic biosensors, genosensors, immune sensors, etc. Biosensors can be also divided into several categories based on the transduction process, such as electrochemical, optical, piezoelectric, and thermal or calorimetric biosensors [1]. Particularly, enzyme-based electrochemical biosensors are attracting ever-increasing attention due to their potential applications in many areas. Nanostructured materials have received much attention because of their novel properties, which differ from those of bulk materials. Control of dimension and morphology of materials has aroused the interest of researchers in the design of functional devices due to the optical and electronic properties of nanometer- and micrometer-sized materials, which determine their applications, can be adapted by varying their size and shape [2].ZnO a versatile semiconductor material, has been attracting attention because of the commercial demand for optoelectronic devices operating at blue and ultraviolet regions. ZnO is a wurtzite –type semiconductor with band gap energy of 3.37eV and it has very large excitation binding energy (60meV) at room temperature. ZnO plays an important role in optics, optoelectronics, sensors, and actuators due to its semi conducting, piezoelectric, and pyroelectric properties. Nano structured ZnO not only possesses high surface area, good biocompatibility and chemical stability and is non-toxic, but it also shows biomimetic and high electron communication features [3]. Recent advances in biocompatible nano materials and biotechnology open a promising field toward the development of enzyme- based biosensors [4]. Sensors are a class of devices that produce measurable responses to changes in physical conditions or chemical concentrations. In general, a sensor comprises sensing elements and signal transducer, and produces signal properties of high sensitivity, fast responds and low cost, the sensors continue to make significant impact, especially in biological and medical applications [5]. To develop ZnO as an optical sensing platform, the nano-micro surface first must be chemically altered for bimolecular complexes. Surface modification should encompass UV and / or visible emission stabilization and some level of chemical functionality for subsequent bio-or chemical conjugation [6]. Our work are approach addresses with this issues and focuses on the ZnO M/NP synthesis and characterization its properties that may lead to improvements in material properties for specified applications to present preliminary results which in this approach could be a way to develop ZnO biosensor devices and using polyaniline (PANi) with ZnO particles as conducting polymer . Metal oxide /polyaniline composite have been for preparation of flexible nano/micro generator. Metal oxide and a p-type conjugate polymer and explore the possibility for the formation of p-n junction [7].

SYNTHESIS OF ZNO N/MPS

To prepare the ZnO nano/micro particles, in typical experiment, a 0.45M aqueous solution of zinc nitrate (Zn $(NO_3)_2.4H_2O$) and 0.9 M aqueous solution of sodium hydroxide (NaOH) were prepared in distilled water. Then, the beaker

contains NaOH solution was heated at the temperature of about 55^{o}C. The Zn $(NO_3)_2$ solution was added drop wise slowly for 60 min to the about heated solution under high speed stirring. The beaker was sealed at this condition for 2 h. The precipitation ZnO N/MPS was cleaned with deionized water and ethanol then dried in air atmosphere at about 60^{o}C [1]. Typically, 100 mg prepared ZnO was mixed in aniline (2 ml)/ methanol (5 ml) solution mixture. The resulting mixture was stirred for 1 h at room temperature on a magnetic stirrer and finally a transparent solution was obtained. In this solution, 5 ml of 0.5M aqueous $CuSO_4$ solution was added drop by drop with constant stirring at 25 ^{O}C for 3 h. A dark blackish green color precipitate was collected at the end of reaction. The precipitate was allowed to settle, filtered and dried at 25 ^{O}C for 6 h [7]. (PANi) added with ZnO particles as conducting polymer and the mixture are deposited on glass.

RESULT AND DISCUSSIONS

X- ray diffraction spectra

X-ray diffraction analysis, obtained for 2θ scan between 30^{o} and 50^{o} at 0.0500^{o} glancing angle, indicated that the deposited ZnO films on the glass substrate were polycrystalline and retained a hexagonal structure type wurtzite. The diffraction peaks are easily indexed on the basis of the hexagonal structure of ZnO ($P6_3mc$ (186), a=3.24982A^{o}, and c=5.20661 A^{o}, (JCPDS v.1.30). Miller indices are indicated on each diffraction peak. It can be seen that a set of peaks with strong intensity can be obtained and its position refers to a crystalline ZnO phase, It is seen that the reflection for the parent residual organic compound disappear completely, whereas the (100), (002), (101) and (102) reflections peaks are observed at 2θ= (32.33, 34.50, 36.3 and 47.9 degree) respectively for hexagonal ZnO. These results are closely with other with other research [8].

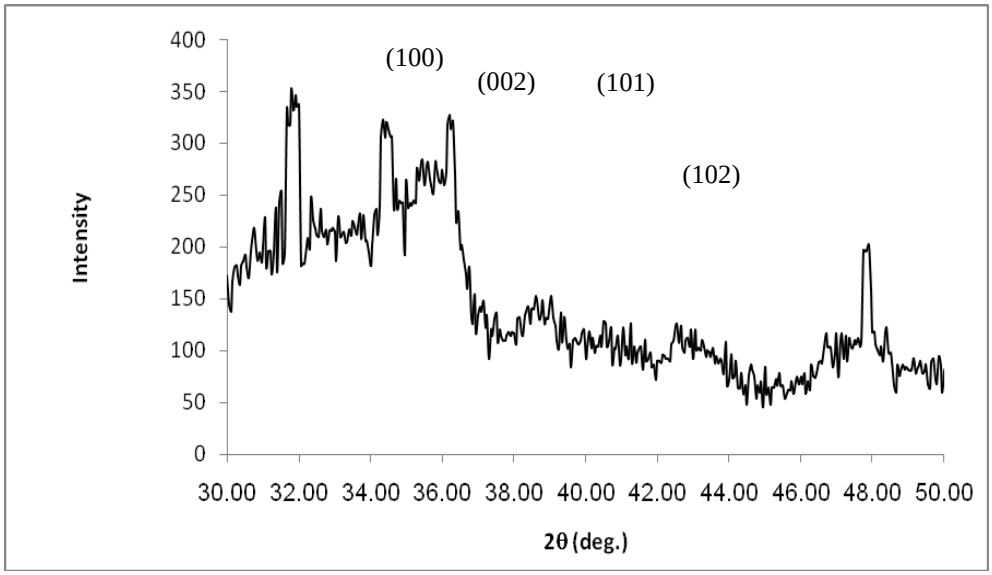


Figure (1) X-ray diffraction (XRD) of ZnO powder sample.

FTIR spectroscopy supplements the information obtained from XRD. It is combination of all data and helps us to understand, analyze and refined more effectively the structure of ZnO in addition it insures us of our procedure of preparation ZnO powder. Figure (2) shows the FTIR transmittance spectra of ZnO sample. The FTIR spectrum of synthetic ZnO powder showed main absorption bands due to O-H stretching of hydroxyl group at 3373 cm^{-1}, O-H bending of hydroxyl group at 707 cm^{-1} and Zn-O stretching of ZnO at 466cm^{-1}. These data are similar to the result of another study [9].

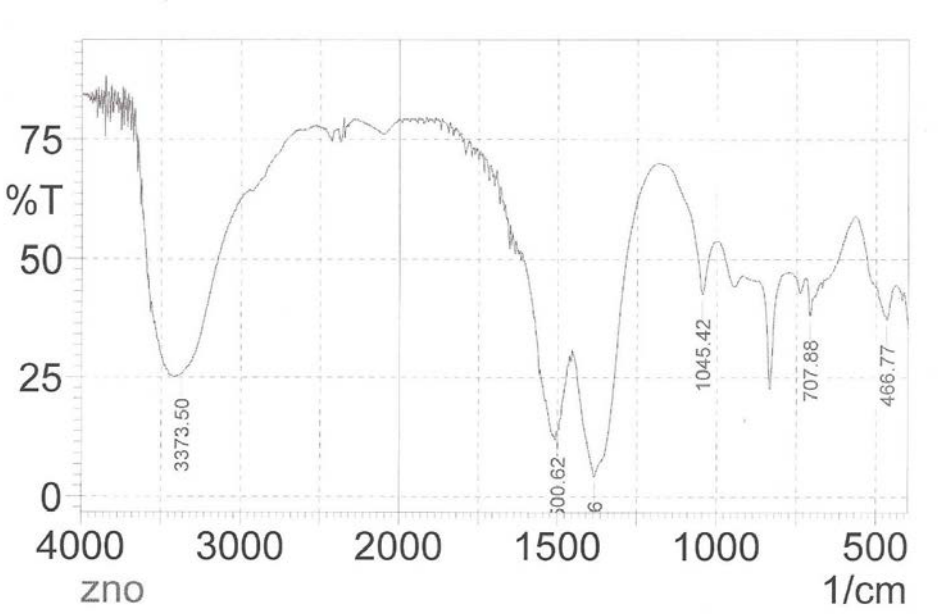


Figure (2) FTIR transmission spectra of ZnO Nano/micro powders sample.

The elements present in the ZnO powder were analyzed by using the x-ray fluorescence source, model "SPECTRO X-LAB" with silicon drift, lithium resolution was used for elements analysis from 11Na to ^{92}U non-destructively, the detector resolution was 45eV at energy of 5.9keV of the iron isotopic Fe^{55}. The XRF unite have three target x-ray tube that covers a wide range of x-ray energies. The concentration of elements are as shown in Figure (3), we found that Zinc (Zn) are 43.40% from the peak that appear in chart and oxygen (O) which is not appear in this chart because oxygen atomic number is (8) so the residual amount of oxygen is about 56.1302%, and very small percentage amount of elements as impurities.

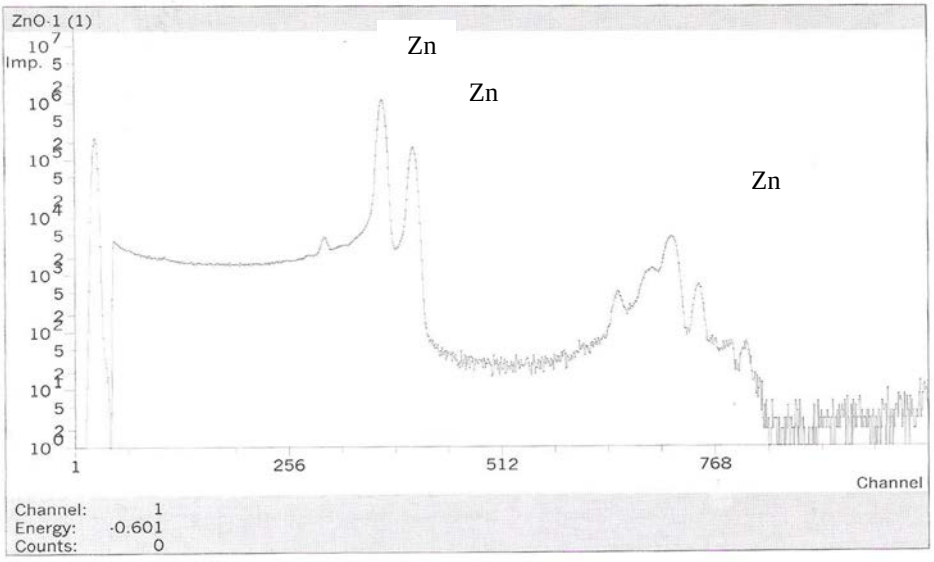


Figure (3) XRF spectra of ZnO Nano/micro particles sample.

Particle Size Distribution (Pzd)

These measurements are used to recognize the particle size distribution of the ZnO powder using "SHIMADZU SALD-2101 –WEA1:V1.20" model. It is found that the particles size of powder are as it shown in Figure (4: a,b).

The size of distributions of ZnO powder particles are depicted in the histogram in Figure (4: a, b), particles size is plotted on the X-axis and the percentage of particles is encountered by the laser beam in the suspension on the Y –axis, our results of this distribution particles diameter are from the range of 188.947 µm to 0.365 µm before cleaning the powder with deionized water and ethanol, and 12.601 µm to 0.297 µm after cleaning with a good percentage of this particles.

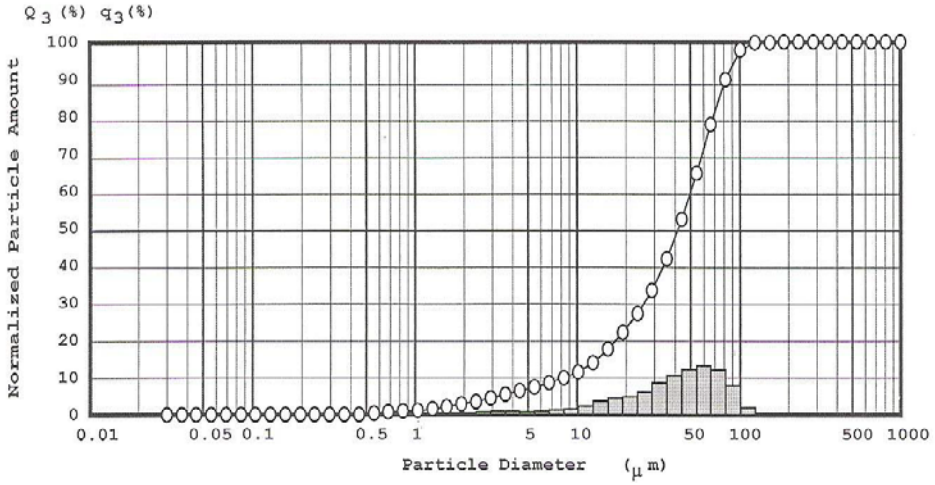


Figure (4 a) PDZ spectra of ZnO Nano/micro powder sample before cleaning.

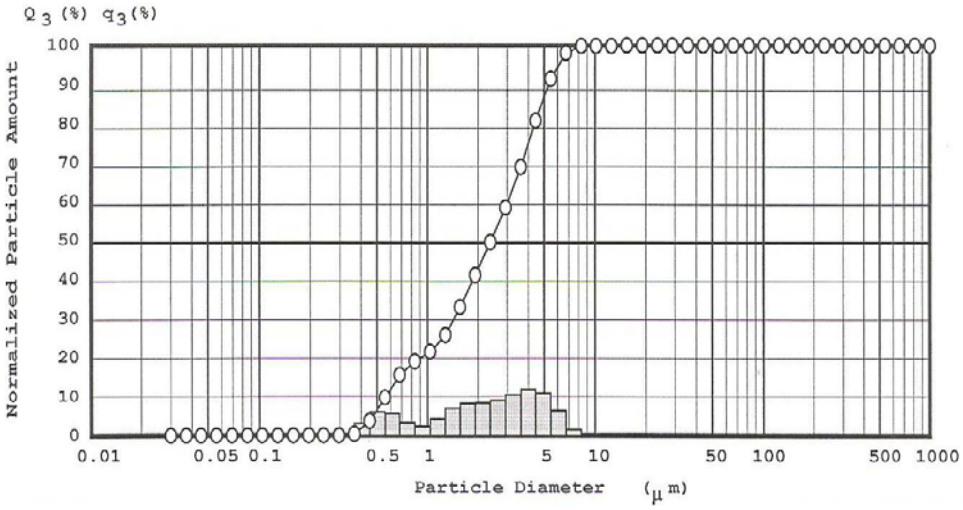


Figure (4 b) PDZ spectra of ZnO Nano/micro particles sample after cleaning.

Structure and morphology

The ZnO samples morphology was examined using an optical transmittance microscope (OTM). The ZnO micro/nano powder products synthesized by the source of Zn $(NO_3)_2.4H_2O$ and NaOH in chemical bath solution with different magnifications, the structure of the deposited film is looks like spikes structures which are represented in Figure (5a, b, c, d).

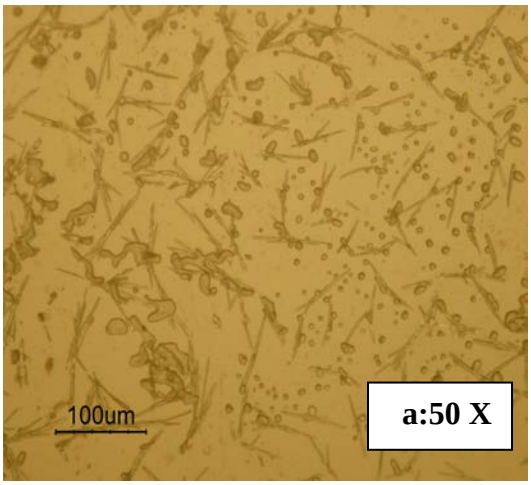


Figure (5) To be continued

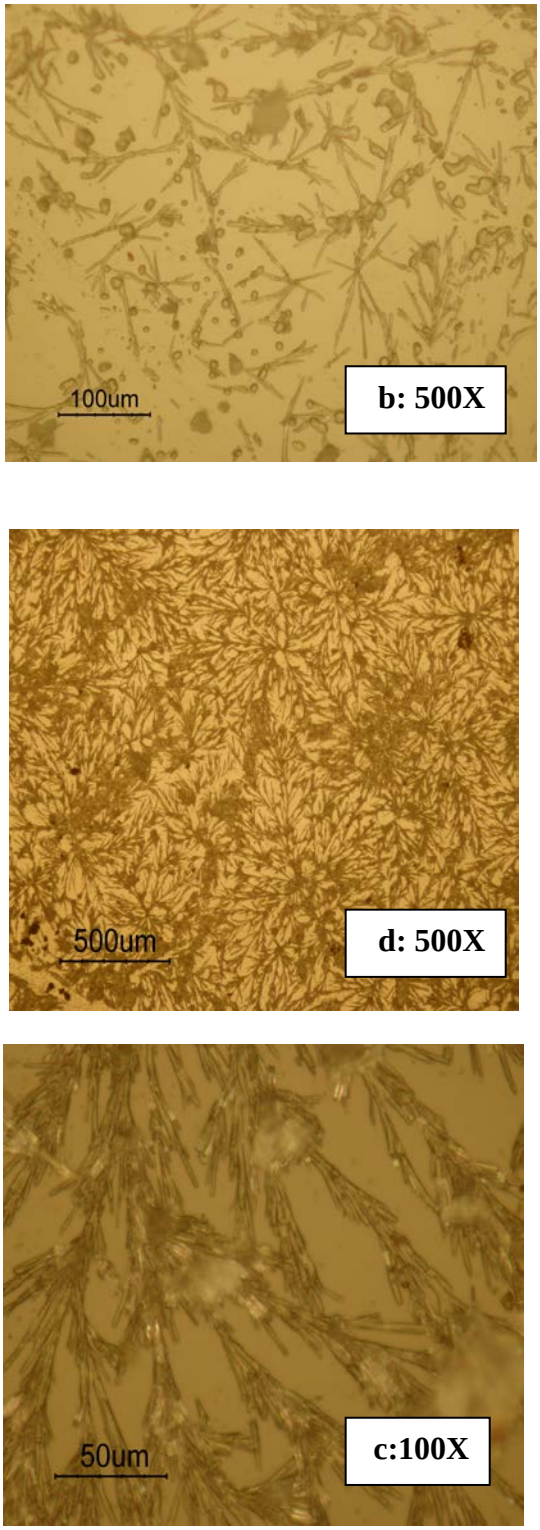


Figure (5 a,b,c,d) OTM images of ZnO nano/micro particles deposited on glass products synthesized by the source of $Zn(NO_3)_2.4H_2O$ and NaOH in chemical bath solution with different magnifications.

Optical Properties

Figure (6 a and b) shows the and transmission and absorbance in UV-visible spectra region for ZnO, measured transmittance in the rage 200nm to 1200 nm. The higher transmission in for ZnO as shows in Figure (6a). While the spectra revealed that the ZnO films have low absorbance in the visible region as shown in Figure (6b).

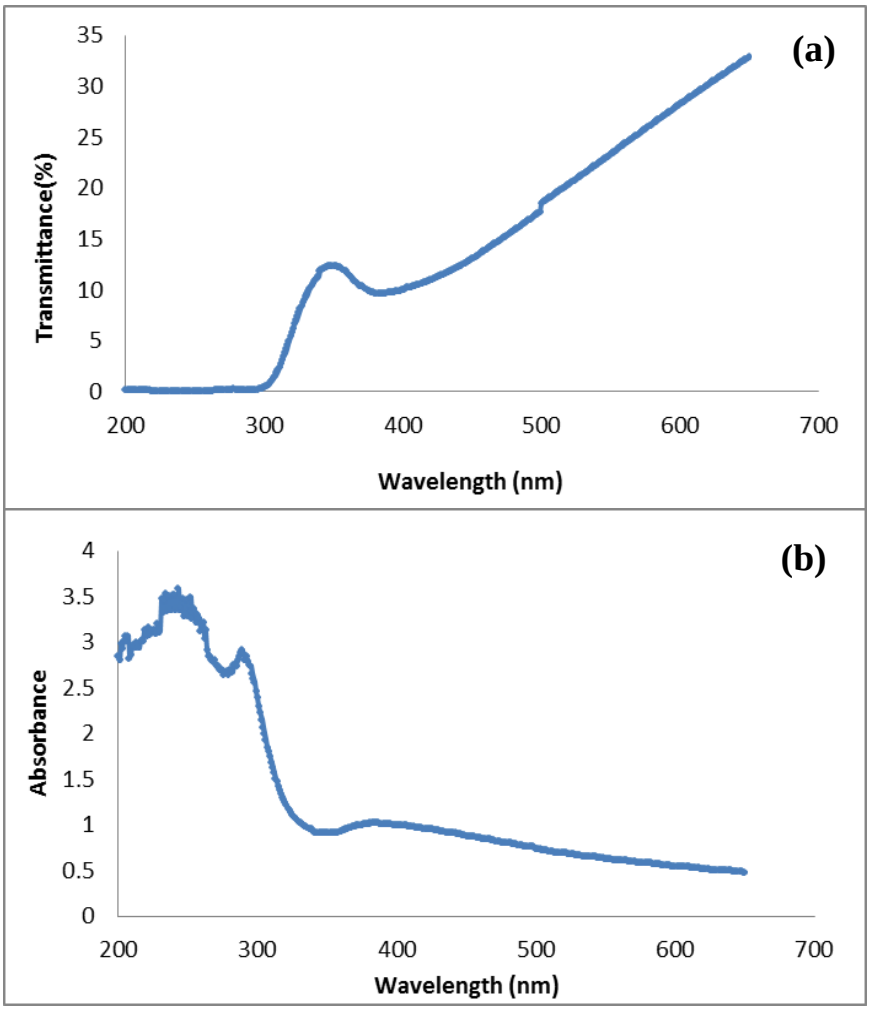


Figure (6a,b) Transmittance and absorbance of spectroscopy of ZnO particles deposited on glass .

The variation of the absorption coefficient (α) with wavelength for the ZnO films is shown in Figure (7a). The absorption coefficient was found to follow the relation [10],[11]. The energy gap Eg was calculated using the relation $(\alpha h\nu)^2=A(h\upsilon - Eg)^n$, $(\alpha h\nu)^2$ as a function of hν [12], where α is the absorbent coefficient of the thin film and A is a constant, hν is the photon energy of the

incident light, n is an integer which depends on the nature of transition. For direct transitions n = ½ or $^{2}/_{3}$ while for indirect n = 2 or 3 depending on whether they are allowed. The band gap Eg can be obtained by extrapolating the linear portion to the photon shown in Figure (7b).The value of energy gap (3.8eV).

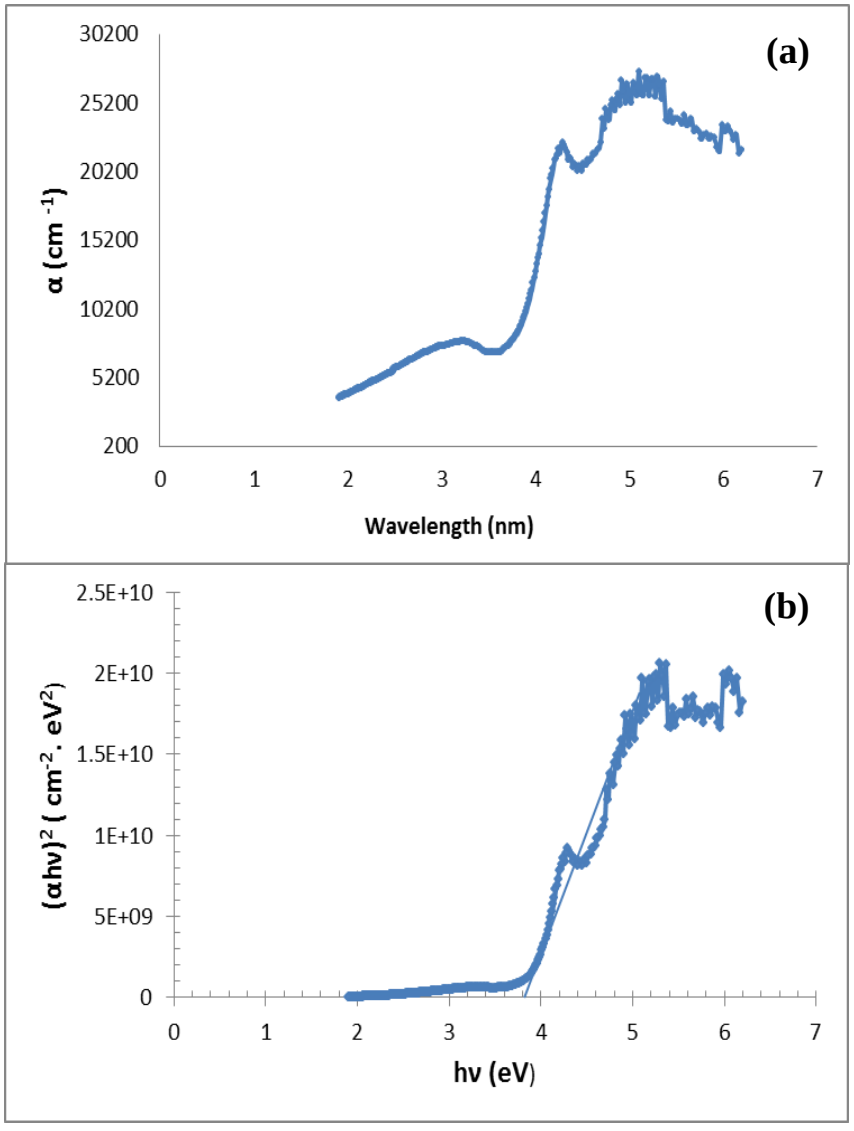


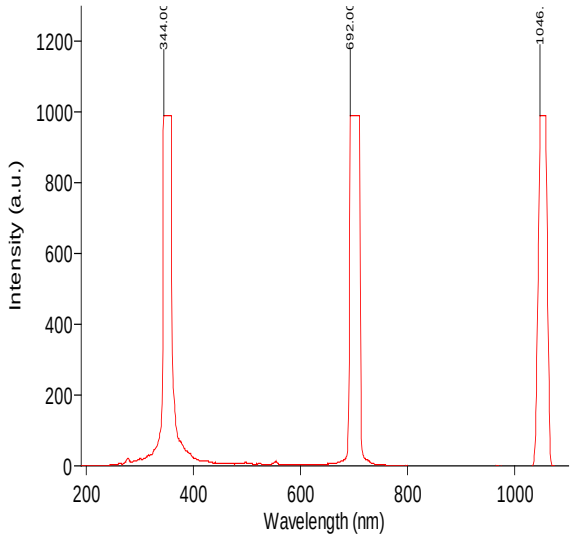
Figure (7a) Absorption coefficient vs. wave length, b. $(\alpha h\upsilon)^2$ vs. hυ for ZnO particles deposited on glass.

Photoluminescence of PANi , ZnO/PANi composite

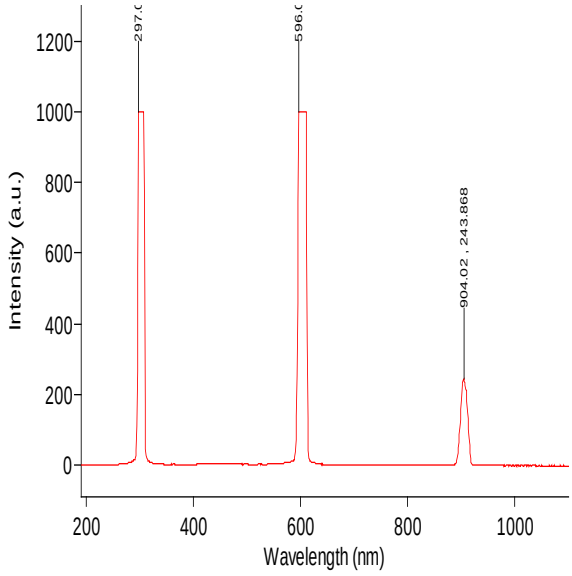
The spectrophotometer, VARIAN, CARY Eclipse from 190-1100nm was used to major peaks in both PANi and with ZnO/ PANi composite as it shown in Figure (7 a, b). The photo luminescence signal consists of two emission peaks, one peak is in the UV- and other is in the visible region as is listed in Table (1). The UV-VIS spectra encouraged us to understand the electrical conductance behavior of composite materials, The shift in peaks in composite shifted than pure PANi is because of composite formation is due to interaction between metal and aniline and supports. Thus it confirms the interaction between ZnO and PANi Matrix, since ZnO is nonmetallic (lewis acid) in nature and aniline is weak base. Thus aniline donates a lone pair of electron towards ZnO and forms complex type structure due nonmetallic (lewis acid) nature of ZnO and basic nature of aniline. It forms ionized polymeric chain and produces efficient switching effect in materials *[7]* .

Table (1) Major peaks of PANi and ZnO /PANi composite in PL spectrum.

Materials	Emission peaks positions (nm)	
	Ist	**II^{n}**
PANi	**344**	**692**
ZnO/PANi	**297**	**596**



a: The emission peaks of /PANi



b: The emissiom peaks of ZnO/PANi compasite

Figure (7 a, b) Photo luminescence of PANi, ZnO/PANi compasite sample.

CONCLUSIONS

In summary, N/MPs ZnO have been grown via a chemical bath deposition process using a 0.45M aqueous solution of zinc nitrate ($Zn(NO_3)_2.4H_2O$) and 0.9 M aqueous solution of sodium hydroxide (NaOH). The XRD characterizations showed that ZnO nano/micro particles were highly crystalline with hexagonal phase. From OTM characterizations , ZnO N/MPs was seen as to be wires tube with rang ~ between 180-350nm .The PL peaks Of ZnO/PANi refers to introduction of chemical functionally and retention of re activity illustrate our ability to create a platform for forming biosensor on the N/M ZnO surface . This optically responsive bio sensing platform can serve as template for immobilizing antibodies, anzymes, etc.

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