

**Synthesis of nanorod ZnO-In<sub>2</sub>O<sub>3</sub> as instant response UV  
photoconductor**

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**Abstract:**

ZnO nanorods were prepared by hydrothermal method and In<sub>2</sub>O<sub>3</sub> nanoparticles prepared by sol-gel method were mixed with ZnO nanorods by weight (90%ZnO+10%In<sub>2</sub>O<sub>3</sub>) and (80%ZnO+20%In<sub>2</sub>O<sub>3</sub>). ZnO and ZnO - In<sub>2</sub>O<sub>3</sub> thick films have been prepared by screen printing and firing at 550°C for 3hours. All the prepared samples were characterized by field emission scanning microscope (FESEM) ,the results showed that ZnO nanorods was covered by In<sub>2</sub>O<sub>3</sub> nanoparticles and the covering was increased with In<sub>2</sub>O<sub>3</sub> percentage increased , X-Ray diffraction (XRD) result shows that the crystallite size of ZnO nanorods ware about (68.1 nm ) also crystallite size decreased when In<sub>2</sub>O<sub>3</sub> weight increasing , From photoluminescence (PL) results it was observed that blue shift was happened when In<sub>2</sub>O<sub>3</sub> was added , photoconducting measurement were showed blue shift and response time in the UV range was increase with increasing In<sub>2</sub>O<sub>3</sub> nanoparticles .

**تحضير القضبان النانوية ZnO-In<sub>2</sub>O<sub>3</sub> كموصل ضوئي UV**

**لحضي الاستجابة**

**أ. م . د . رعد سعدون صبري**

**الخلاصة :**

تم تحضير القضبان النانوية لأكسيد الخارصين بطريقة الهيدروثيرمل وكذلك تحضير الجسيمات النانوية لأكسيد الانديوم بطريقة المحلول-الغروي حيث تم مزجها مع لأكسيد الخارصين النانوي بنسب وزنية (90 % ZnO + 10 % In<sub>2</sub>O<sub>3</sub>) و (80% ZnO + 20%In<sub>2</sub>O<sub>3</sub>) وتم تحضير الاغشية السميكة لأكسيد الخارصين و لأكسيد الخارصين - اوكسيد الانديوم بطريقة طباعة

الشاشة وبدرجة حرق  $550^{\circ}\text{C}$  ولمدة 3 ساعات وتم فحص جميع النماذج باستخدام المجهر الإلكتروني الماسح (FESEM) وظهرت النتائج ان القضبان النانوية لل ZnO غطيت بالجسيمات النانوية لأكسيد الانديوم وان التغطية تزداد مع زيادة نسبة اوكسيد الانديوم وظهرت نتائج حيود الاشعة السينية (XRD) ان الحجم البلوري لأكسيد الخارصين هو تقريبا (68.1nm) وكذلك فأن التبلور يتناقص مع زيادة نسبة اوكسيد الانديوم ومن محصلة التلؤلؤ الضوئي (PL) لوحظ ان هناك انحراف باتجاه الازرق مع زيادة نسبة اوكسيد الانديوم وكذلك بينت نتائج التوصيلية الضوئية ان هناك زيادة كبيرة في سرعة الاستجابة للضوء فوق البنفسجي (UV) تزداد مع زيادة نسبة اوكسيد الانديوم.

## **1. Introduction**

Metal oxide thick films have been traditionally used in different devices like sensors, piezoelectric and optoelectronic devices [1], transparent oxide semiconductors have attract a great deal of attention for many application such as transparent thin film transistors ( TTFT<sub>s</sub>) [2,3] solar cell [4] detectors and sensors [5,6]etc, ZnO is an remarkable II-VI compound semiconductor which have wide band gap ( 3.37 eV ) also have high exciton binding energy (60meV) [7],it's have many nanostructures such as nanotube, nanorod, nanoflower...etc, have been synthesized through various methods have been used to synthesis pure and doped ZnO films such as chemical spray pyrolysis, thermal vacuum evaporation, chemical vapor deposition ,hydrothermal, sputtering, pulsed laser ablation , sol-gel [8,9] method and others, hydrothermal and simple evaporation are most prevalent and promising methods for the synthesis of isometric ZnO nanostructures , these methods have many advantages such as low cost , simple and one-step synthesis without any additional processes like catalyst , template or buffer layer [7,10].Trivalent element such as Al, Ga and In are predominantly used to precisely control the electrical conductivities for optoelectronic device application [11].

Recent research has been oriented towards nanocrystalline materials that provide a huge increase in the surface to volume ratio for a material ,high surface area and controlled structure is target in most researches due to the enhancement of performance devices and application , screen printing technique was introduced to produce compact and relatively inexpensive hybrid circuit for many purpose ,In this paper we report ,a nano heterostructure of ZnO - In<sub>2</sub>O<sub>3</sub> by very simple method and study its structural ,morphology and photoconductive UV detector.

## **2. Experimental Details:**

### **2.1. ZnO nanorod preparation:**

ZnO nanorod was prepared using aqueous solutions of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (>99% sharlu, Spain), hexamethylenetetramine  $\text{C}_6\text{H}_{12}\text{N}_4$  (HMT) (>99% Aldrich Germany). 0.07M of aqueous solution was prepared by dissolved in de-ionized water in a glass beaker under stirring without heating for 15 min until the solution became transparent. When it became transparent, the solution transferred in to glass autoclave of volume 90 ml in addition, the autoclave was closed firmly and putted in oven and kept at 80 °C for 5 hours. Finally the autoclave cooled down naturally and gradually about 12h (cooling time). As a result white powder was Precipitate in the bottom of autoclave. In order to remove any contamination from the powder, the collected powder washed four times in ethanol and distilled water and dried in air.

### **2.2. Preparation of $\text{In}_2\text{O}_3$ nanoparticles :**

Growth of  $\text{In}_2\text{O}_3$  nanoparticles was performed by using sol-gel method,  $\text{In}(\text{NO}_3)_3$  (99.99%) (Alfa Asear) and sodium hydroxide NaOH (99%) (Merck) were used (2mmol) of  $\text{In}(\text{NO}_3)_3$  and (6mmol) of NaOH were dissolved in 30 ml deionized water Then, 1.5 g PVA were added to the solution and stirred at 80 °C for (90min ) to become homogenous solution (sol) and then was converted to a viscose gel, The obtained gel was calcinated in a tube furnace by heating at 500 °C for 2h and  $\text{In}_2\text{O}_3$  nanoparticles resulted

### **2.3. ZnO - $\text{In}_2\text{O}_3$ thick film preparation:**

After production of ZnO nanorods and  $\text{In}_2\text{O}_3$  nanoparticles powders ,the powders were mixed by weight (90%ZnO+10% $\text{In}_2\text{O}_3$ ) (sample (A)) and (20%ZnO+20% $\text{In}_2\text{O}_3$ ) (sample (B)), the product powders were mixed with ethanol under intense magnetic stirring for 3h , then it is dried at 90 °C in air, a few drops of PVA as organic binder was used to make  $\text{In}_2\text{O}_3$ -ZnO-PVA paste ,this paste was prepared in an agate mortar and thoroughly mixing it ,the prepared paste was screen printed on a cleaning and etching Si and glass substrate of size (1 cm<sup>2</sup>) then dried in air for 24h. The prepared thick films were heated in a furnace at 550 °C with a rate of 5 °C /min for 2 hrs.

For electrical and photoconductor measurements the front microelectrodes (IDE) of silver paint were formed by using screen print method, then the films were subjected to heating 70 °C for 20 min. morphologies and microstructures of the prepared samples were characterized by using X-ray

diffraction (XRD, Philips Cu,  $K\alpha$  ) and field emission scanning electron Microscope (Hitachi S-4160 FESEM Japan ), photoluminescence (PL) studies were performed using (Schimadzu, Spectrophotometer Japan, Luminescence Excitation wavelength 325nm) at room temperature ,UV. Photoconductivity measured by using 150Watt Xe –Lampe with monochrometer to obtained a mono wavelength and (Keithly 2430, USA) electrometer used to measuring a change in resistance.

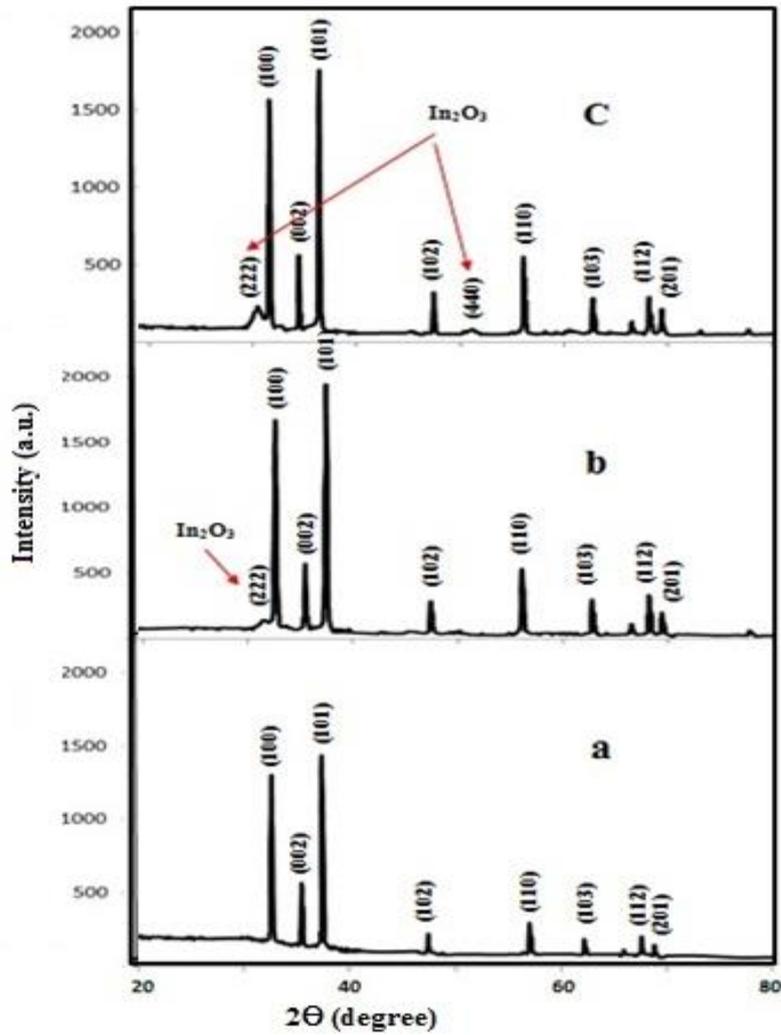
### 3. Result and Discussion

Figure (1) shows the (XRD) pattern of (a) ZnO (b) sample A (c) sample B , XRD spectra show highly crystalline structure in the samples ,as shown in this spectra a mixed phase of cubic  $In_2O_3$  and wurtzite ZnO, the main peaks in both spectra (b,c) were due to ZnO nanorod while the peak at around ( $2\theta = 30.72$ ) were due to  $In_2O_3$  nanoparticles , from the figure it can see that the (30.72) peak intensity was increased with ( $In_2O_3$ ) increasing , the crystallite size was estimated by using Scherer's formula [12] :

$$D = \frac{0.9\lambda}{B \cos\theta} \dots\dots(1)$$

Where  $\lambda$  is the X-ray wavelength and B is the full width half maximum Intensity, the crystallite size was decreased with ( $In_2O_3$ ) increases as shown in Table (1),this result was agreement with [13, 14] .

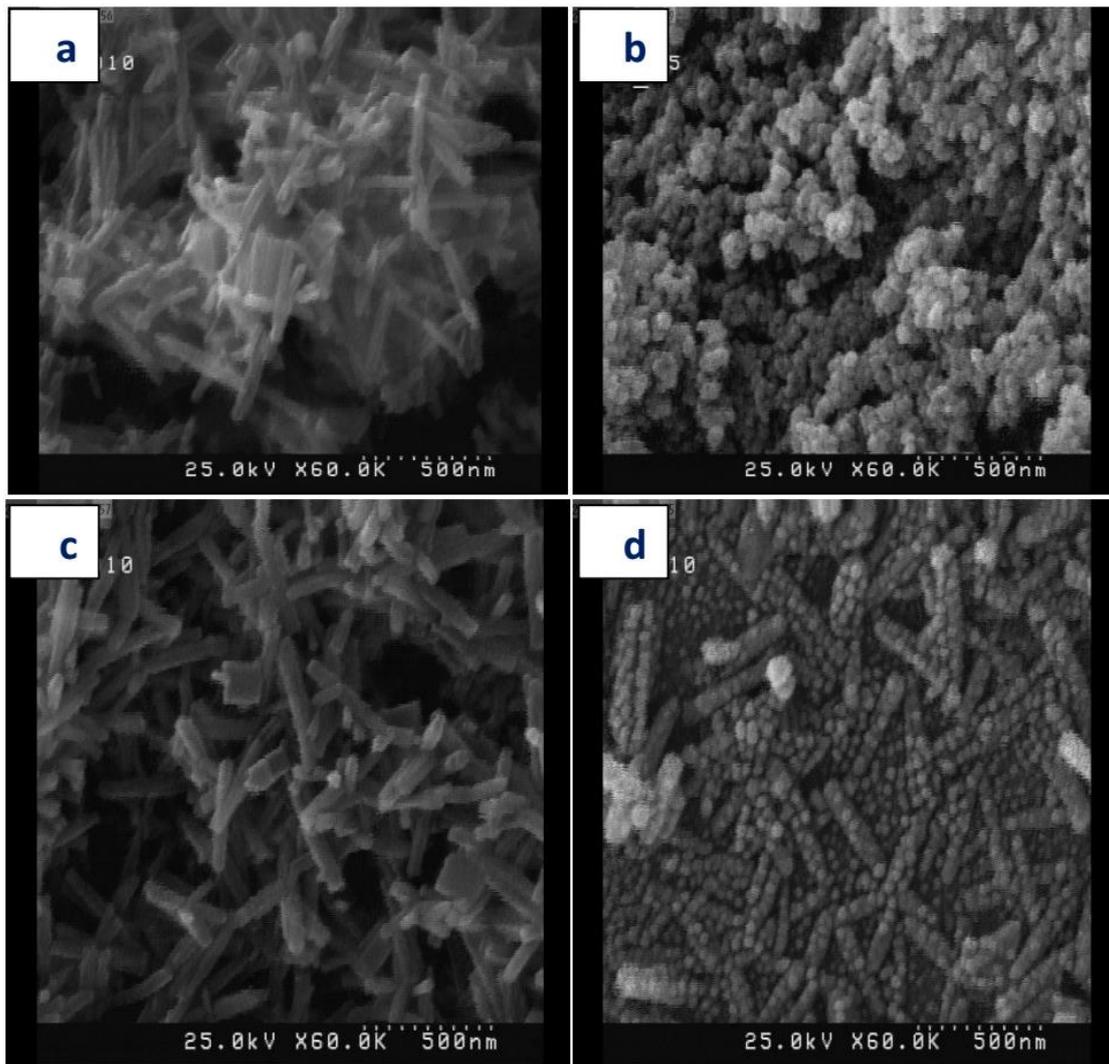
The FESEM images are shown in figure (2) image (a) show the ZnO nanorod prepared by hydrothermal method a rods have average length about 370nm and radius about 35 nm, image (b) show the  $In_2O_3$  nanoparticles with about 38 nm average grain size, we can easily find out the ZnO- $In_2O_3$  nano heterostructures in images (c,d) ,from this images we can see that the ZnO rods was covered by  $In_2O_3$  nanoparticles .



**Fig.1: XRD pattern of as prepared samples (a) ZnO (b) sample A (c) sample B**

**Table (1): the crystallite size of as prepared samples.**

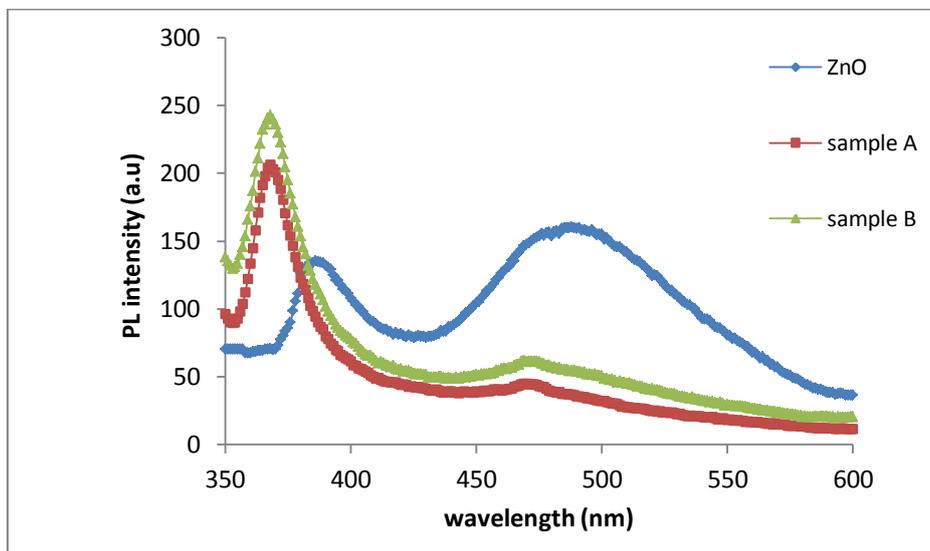
Samples	Average crystallite size nm
ZnO	68.1
A	57.9
B	52.4



**Fig. 2. FE-SEM images of (a)ZnO , (b) In<sub>2</sub>O<sub>3</sub> , (c) sample A (d) sample B**

Photoluminescent (PL) study is very important method to investigating the effects of maxing or doped on the optical properties of ZnO nanostructures because doped ZnO nanostructures are expected to have different optical properties in comparison with pure ZnO[13],The room temperature PL spectra of ZnO- In<sub>2</sub>O<sub>3</sub> Nano rods are shown in figure (3) for ZnO PL there are two distinguished peaks centered around (370nm) and (486nm ) respectively, strong peak in the ultra violet region (UV) (370nm) it's well known that originates from near band-edge (NBE) emission from the recombination of free excitons [15,16] ,another weak and broad green peak deep-level emission (DLE) around (485nm) assigned to the ionized oxygen vacancies through the recombinant of photon – generated hole and electrons occupied oxygen vacancy. The PL measurements were carried out at room temperature, it was well known that the bulk In<sub>2</sub>O<sub>3</sub> cannot emit light at room temperature; Here we note the

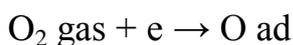
existence of emission at room temperature for  $\text{In}_2\text{O}_3$ . This explains because of PL mechanism was related to quantum confinement effect [17, 18]. Both (A and B) samples showed two emission peaks centered at (368nm) and (488nm) as shown in figure (3) in which the peak at 368nm was corresponding to (NBE) emission, the blue shifted in (NBE) emission can be refer to quantum confinement which happen because the reducing in particle size as a result to  $\text{In}_2\text{O}_3$  added, while at 488nm was corresponding the characteristic green emission. It was clear from the figure that the intensity of the two peaks for 20% $\text{In}_2\text{O}_3$  were increasing, also it was signified from the figure that (A and B) have the same peak positions. Also the NBE/DLE ratio increasing when  $\text{In}_2\text{O}_3$  increased refer to enhancement in crystalline quality which agreement with previous works for ZnO nano heterostructures [13, 19]



**Fig.3: PL spectra of as prepared samples.**

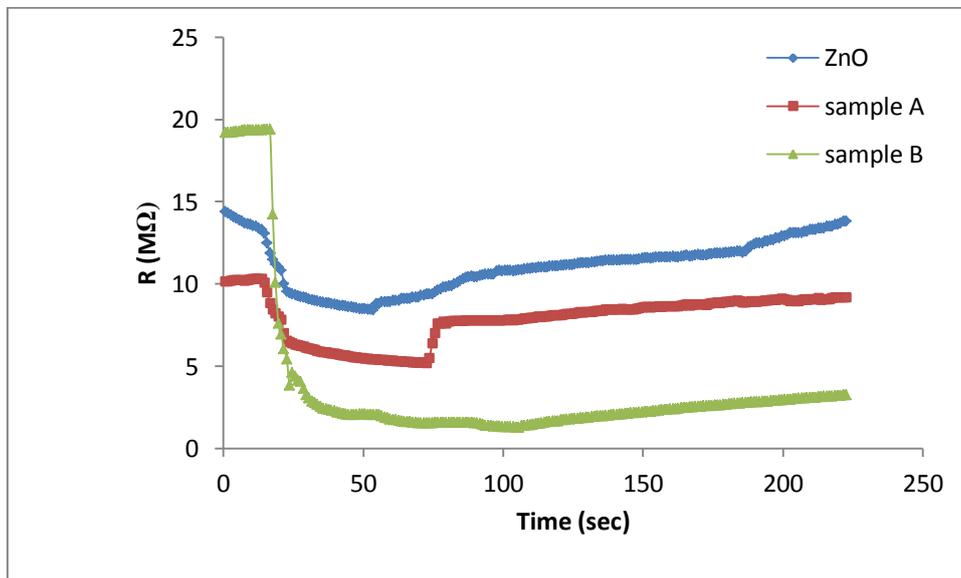
### 3.1. Photoconduction properties:

The photo detection could be influenced by oxygen molecules adsorbed on the surface of nanorods decreases the carrier's density by captured/deprived the free electrons:



This reduces the net carrier density in the nanorods, the ultraviolet response time is dominating by adsorption and desorption of  $\text{O}_2$  molecules on the surface. when the sample was exposed to UV illumination the electron–hole pairs well be generated under irradiation by photon energy greater

than the band gap after that the holes migrate to the surface of the sample then react with oxygen ions this lead to decrease the depletion layer near the surface at the same time the electrons resulted from UV generated electron-hole pairs become free this will contribute to the increases the current this meaning a decrease of the resistance value. When the UV light turn off the holes recombines with electrons this result in an increase of the resistance value. Figure (4) shows the variation of resistance with time (without applied bias), from this figure we can see that the resistance was decrease when the samples was exposed to (370 nm) UV illumination, good response was observed in the UV region, the minimum resistance value was obtained after 10 sec response time for ZnO ,while its increased for sample A to 14 sec ,but for sample B we observed dramatic change happen, its clear from the figure that fast drop of resistance occur when UV light exposed to the sample, the response time decreased to about 5 sec this result can be explained as follows : the first reason is decreased the crystalline size and enhancement in structure when  $\text{In}_2\text{O}_3$  increased as the structural and PL result showed this lead to decreased the defects and reduced the recombination effect ,the second reason is increased the surface to volume ratio as clear in FESEM result thus increasing the number of absorption photon which mean increasing the photoconductivity .



**Fig.4: variation of resistance with time at UV illumination.**

#### **4. Conclusions:**

ZnO- $\text{In}_2\text{O}_3$  nano heterostructures were successfully synthesis by mixing of ZnO nanorods with  $\text{In}_2\text{O}_3$  nanoparticles. X-Ray diffraction (XRD), FESEM images, photoluminescence (PL) results shows , when  $\text{In}_2\text{O}_3$  nanoparticles

covered the ZnO rods, the UV photoconductivity was increasing also when the In<sub>2</sub>O<sub>3</sub> nanoparticles increase the short and Sharp response time was obtained, that means it is suitable for photoelectronic and UV detection.

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