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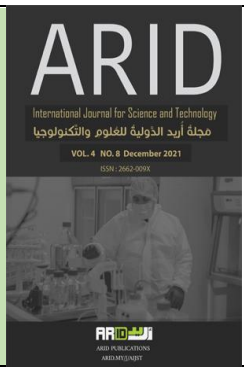

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Preparation and Characterization ZnO Nanorods for Photocatalyst Application

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تحضير وخصائص قضبان أوكسيد الزنك النانوية وتطبيقاتها كمحفز ضوئي

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Abstract

Zinc oxide (ZnO) nanorods are prepared onto glass substrates via chemical bath deposition method. ZnO nanoparticles is prepared onto glass substrate to act as a seed layer for grown ZnO NRs. Field Emission Scanning Electron Microscope (FESEM) image confirmed that the grown rods have hexagonal shape covered the surface of substrate. Further, the prepared ZnO NRs appeared good crystallinity according to X-ray diffraction method. The absorption edge for seeds nanoparticles layer appeared at wavelength of 362nm (3.42 eV) while it was at around 479nm (3.27 eV) nm for the grown ZnO NRs. The grown ZnO NRs showed two emission peaks at 381nm and 540nm corresponding to near band-to-band electron-hole recombination and oxygen vacancies, respectively. Degradation rate of methylene blue (MB) dye was 0.01% after 1h of illumination by UV light and increased to 71.4% after 4h of illumination.

Keywords: ZnO, Nanorods, methylene blue, photocatalyst.

الملخص:

قضبان أوكسيد الزنك النانوية تم تحضيرها على قواعد زجاجية بطريقة الحمام الكيميائي. دقائق أوكسيد الزنك تم ترسيبها على قواعد الزجاج لتعمل كطبقة بذرات لإنماء قضبان أوكسيد الزنك النانوية. صور المجهر الإلكتروني الماسح أكدت الحصول على تركيب القضبان النانوية لأوكسيد الزنك السداسية الشكل وبتبلورية جيدة بحسب فحوصات حيود الأشعة السينية. حافة الامتصاص البصري لطبقة البذرات كانت عند أطول الموجي (3.42eV) 362 nm بينما كانت عند (3.27 eV) 479 لأغشية قضبان أوكسيد الزنك النانوية. قضبان الزنك النانوية المحضرة أظهرت قمتان لانبعاث الضوء عند 381nm وأخرى عند 540nm تعودان لإعادة الالتحام إلكترون-فجوة والأخرى لفراغات الأوكسجين على الترتيب. نسبة التحلل لصبغة المثيلين الزرقاء كانت 0.01% بعد مدة تشعيع مقدارها ساعة بالأشعة فوق البنفسجية ازدادت لتبلغ 71.4% بعد فترة تشعيع استمرت إلى 4 ساعات.

الكلمات المفتاحية: أوكسيد الزنك، القضبان النانوية، المثلين الزرقاء، المحفز الضوئي.

1. Introduction

Nanomaterials have received much attention because of their unique physical, chemical, and mechanical properties that distinguish them from the bulk-phase materials [1]. One-dimensional (1-D) nanostructures such as nanorods, nanowires, nanotubes, and nanobelts, have attracted much attention and play an interesting role as candidates for future electronic components. The 1-D nanostructures have several unique advantages, such as high surface-to-volume ratio, quantum confinement phenomena, and slow electron–hole recombination [2,3]. Zinc oxide (ZnO) is the most interesting metal oxide semiconductor due to its large bandgap of 3.37 eV and high binding energy of 60 meV [4]. In addition, ZnO nanostructures, such as nanorods and nanowires, have a high-surface-area-to-volume ratio, which is the most significant property of ZnO nanostructures that are used for many of applications such as gas sensor [5], ultraviolet detector [6,7], Light emitting diode (LED) [8,9]. ZnO nanorods as well as nanowires is prepared through different physical and chemical methods like CVD [10], electrochemical [11], thermal evaporation [12], hydro and solvothermal [13,14]. Among these methods, chemical bath method (CBD) which is a simple and inexpensive to deposit homogeneous and high quality thin films and has been widely used to synthesize nanocrystalline semiconductor thin films [15]. Therefore, CBD is widely used to grow ZnO nanorods onto various substrates [16-18]. One of the most important application of metal oxides semiconductors is photocatalyst that can be used as effective method to remove organic pollutants from water. Photocatalysis process is an abundant green energy source for different application such as hydrogen fuel produced and wastewater treatment by assist of solar radiation. ZnO nanostructure is considered as a promising photocatalytic material due to its high catalytic activity, low cost, environmental friendliness, chemical stability, and easy synthesis in nanostructured forms [19]. In current work, ZnO

nanorods are prepared via CBD method and their morphology, structural, and optical properties are investigated. Photoactivity of the grown ZnO nanorods was tested against methylene blue dye under UV illumination for different exposed time.

2. Experimental part

2.1 Preparation ZnO NRs and characterization

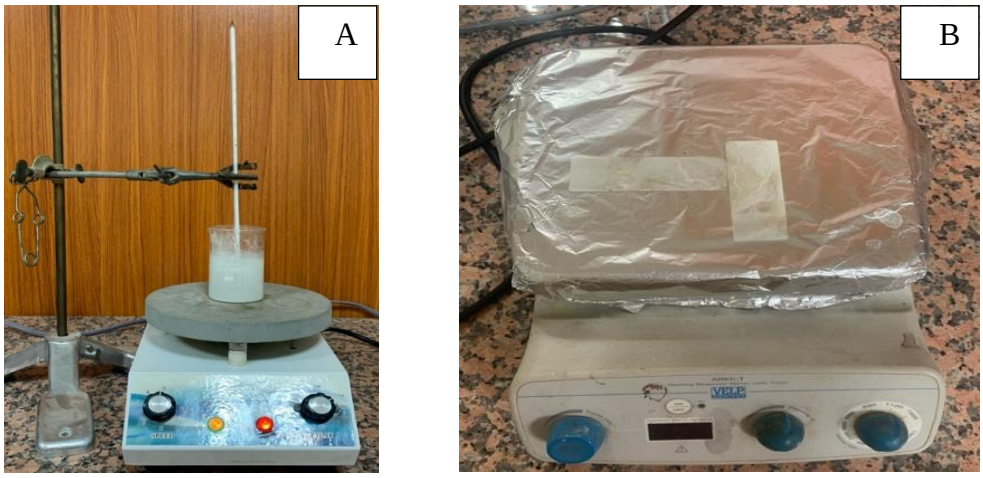
Zinc oxide nanocrystalline thin films are prepared onto glass substrates via chemical bath deposition method. Substrates are cleaned by diluted HCl aced and distilled water (DI) for three times flowed by ethanol for two times and finally by DI with sonication for 15 min. Preparation ZnO nanorods (NRs) onto glass substrate need to ZnO nanoparticles acts as a seed layer [6]. Seed layer was prepared using 0.1M/100 ml H_2O of zinc acetate mixed very well using magnetic stirrer at room temperature for 10 min. Zinc acetate solution is , then, drop casted onto cleaned substrates and heat treated at 300 ^oC for 1 hr to obtain ZnO nanoparticles thin film as shown in Fig.1. To grow ZnO NRs thin films, prepared seeded substrates are immersed inside solution contains 2.9g of zinc nitrate [$Zn(NO_3)_2.6H_2O$] and 1.4g of hexamine ($C_6H_{12}N_4$) that added drop wise with total volume of 100ml H_2O. Temperature is increased gradually to 90 ^oC by hot plate and total preparation time was 2h then samples are removed from the solution, washed by DI and left to dry naturally. The grown ZnO NRs thin films are annealed at 350 ^oC for 1h to enhance their crystallinity and Zn/O ratio stoichiometry. Figure 2A&B shows the solution that used for grow ZnO NRs thin films and prepared samples, respectively. The surface morphology of the prepared samples is studied using a NovaSEM 450 scanning electron microscope (SEM; FEI Co.). The crystalline structure of the prepared samples was investigated using x-ray diffraction (XRD) (PANalytical X'PertPRO with CuKα; 1.5406 A radiation). The optical absorption was investigated using ultraviolet (UV)-visible spectroscopy UV-1800 Shimadzu Co. (Japan) while

the photoluminescence (PL) spectra is investigated by Fluo-Time 300 for Time-Resolved and Steady-State Spectroscopy (Germany) under 360nm excitation light.

2.2 Measurements Photocatalytic activity

The photocatalytic activity of the prepared ZnO NRs was investigated against Methylene blue (MB) dye. A 0.01g of MB is dissolved in 250ml of DI and 50ml of prepared solution was used in every test. The prepared ZnO NRs sample cut into 2.5x2.5 cm immersed in MB solution for different times. The sample is exposed by UV light with 260 nm wavelength for 0-4h and 2ml is taken every 1h to measure the optical absorption.

Figure(1): ZnO seed layer onto glass substrates

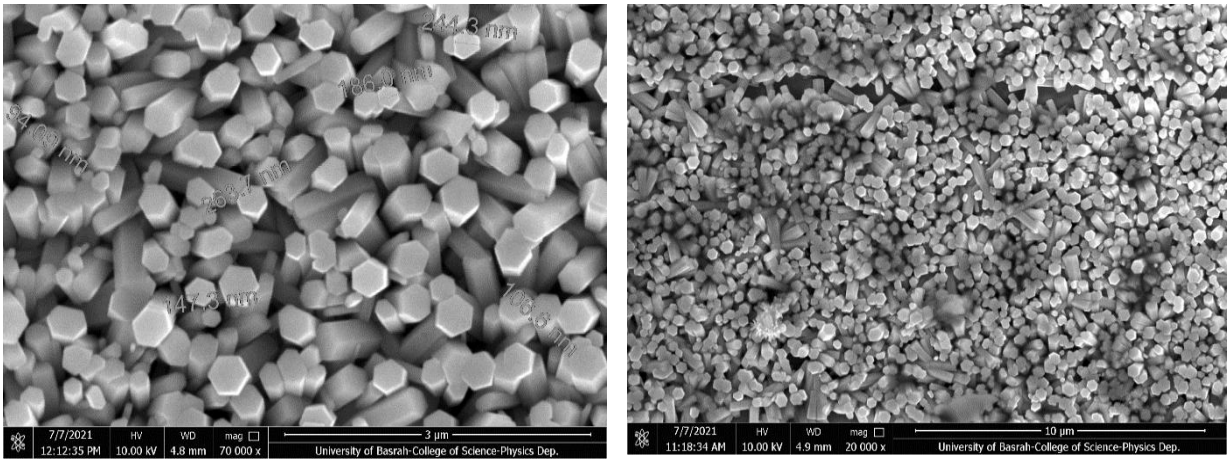


Figure(2): (A) The solution that used for grow ZnO NRs thin films, (B) The prepared ZnO NRs thin films

3. Results and discussion

3.1 Surface morphology

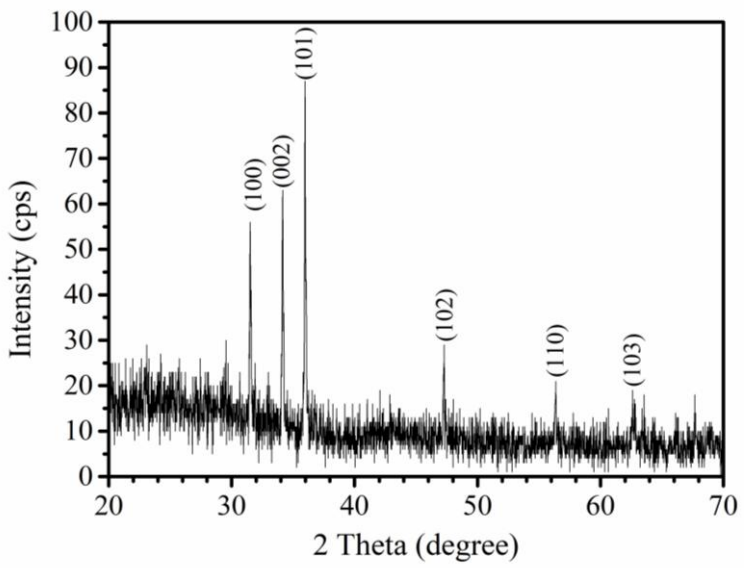
Figure 3 shows the FE-SEM image of prepared ZnO NRs grown onto glass substrates via chemical bath method. The ZnO are structured as hexagonal shaped nanorods covered the surface of substrate. Diameter of the grown ZnO NRs is ranged from 150nm to 260nm. ZnO nanoparticles seeds will act as a centers for grow ZnO NRs and the different in the dimeter of prepared rods is could be due to the seeds aggregated with different size.



Figure(3): FE-SEM image of grown ZnO NRs onto glass substrate via chemical bath deposition

3.2 Crystalline structure

Figure 4 shows the XRD pattern of grown ZnO NRs that prepared onto glass substrate. The pattern appeared in around 6 diffraction peaks at 2θ of 31.5, 34.15, 36.0, 47.3, 56.37, and 62.63 corresponding to (100), (002), (101), (102), (110), and (103) planes of hexagonal ZnO phase. The ZnO NRs is single crystal grown toward (002) crystalline plane, however appearing more than diffraction peak in the XRD pattern is comes from the sides of ZnO NRs where the rods are not growing in alignment vertically on the substrate.

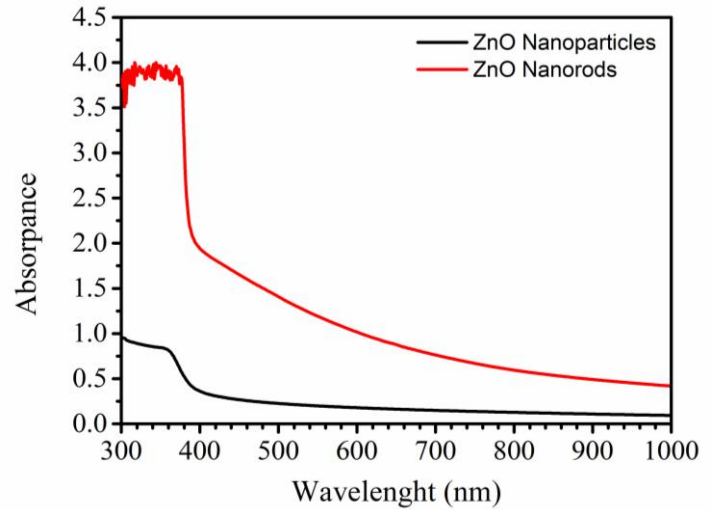


Figure(4): XRD pattern of ZnO NRs grown onto glass substrate via

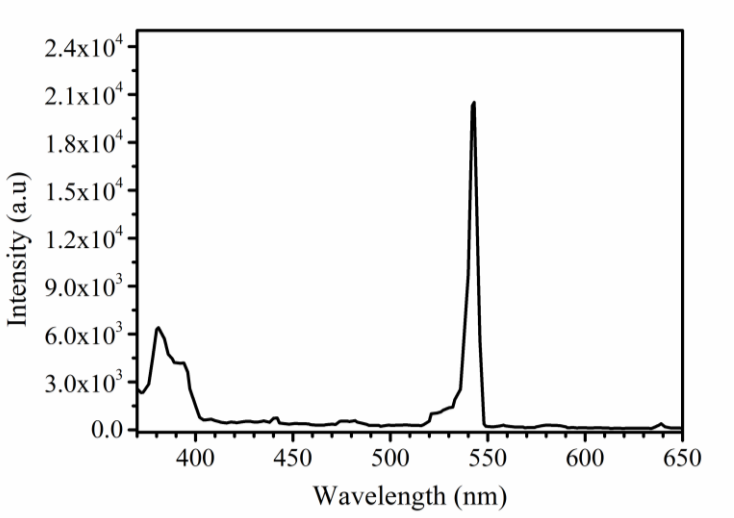
3.3 Optical properties

Figure 5 shows the optical absorption of ZnO seed layer and ZnO NRs thin films that prepared onto glass substrate. The grown ZnO NRs appeared sharp absorption edge compared by ZnO nanoparticles seeds layer due to the different in the thickness as well crystallinity between them. The absorption edge for seeds nanoparticles layer appeared at wavelength of 362nm (3.42 eV) while it was at around 479nm (3.27 eV) nm for the grown ZnO NRs. However, value of

optical band gap is affecting by more than reason such as particles size, shape and the ratio between elements in the compound (Zn/O ratio) thus, obtain band gap in the ZnO seed layer bigger than that for ZnO which could be related those reasons. Photoluminescence (PL) spectrum is shown in Fig.6 and two emission peaks are appeared, abroad one at a wavelength of 381nm and sharp peak at 540nm. However, the emission peak at UV region is corresponding to near band-to-band electron-hole recombination while the other one at visible is related to oxygen vacancies.



Figure(5): Optical absorption of ZnO seed layer and ZnO NRs grown onto glass substrate



Figure(6): Photoluminescence spectrum of ZnO NRs grown onto glass substrate

3.4 Photocatalytic activity

Photocatalytic activity of prepared ZnO NRs is studied through investigating photo degradation of MB dye by measuring the absorbance spectra after exposure by UV light with various times (0-4hr). Figure 7 shows that the absorbance peak decreases with the irradiation time, this indicates a decrease in concentration of MB dye with time. Degradation rate of MB blue dye is calculated using the equation below [19]:

$$Degradation\ rate(\%) = \frac{A_\circ - A}{A_\circ} \times 100, \qquad \ldots.1$$

where A_o, A are the absorbance value before and after exposure by white light for several minutes, respectively. Degradation rate of MB blue dye was just 0.01% after 1h of illumination increased to 1.58% and 3.0% when the time is 2h and 3h, respectively. However, the highest degradation rate was obtained for 4h of illumination with value of 71.4% and it is good result compared by the published literature [20,21]. Dye degradation is happening by photo catalysts when a photon with energy higher than the energy gap illuminates the catalyst leading to excite electrons from valance band (VB) to conduction band (CB) leaving holes. High oxidation potential of holes in CB allows direct oxidation of dye in the reaction medium followed by the degradation process. Dye decay is caused by its interaction with free radicals of hydroxyl (HO·) and superoxide(O2·) that produce by the catalyst according to the interaction that shown by equations [19]:

$$ZnO + h\upsilon \rightarrow ZnO\ (e^-_{CB} + h^+_{VB}) \qquad \ldots\ldots\ldots\ldots \quad 2$$

$$ZnO(h^+) + OH \rightarrow ZnO + OH^{\cdot} \qquad \ldots\ldots\ldots\ldots \quad 3$$

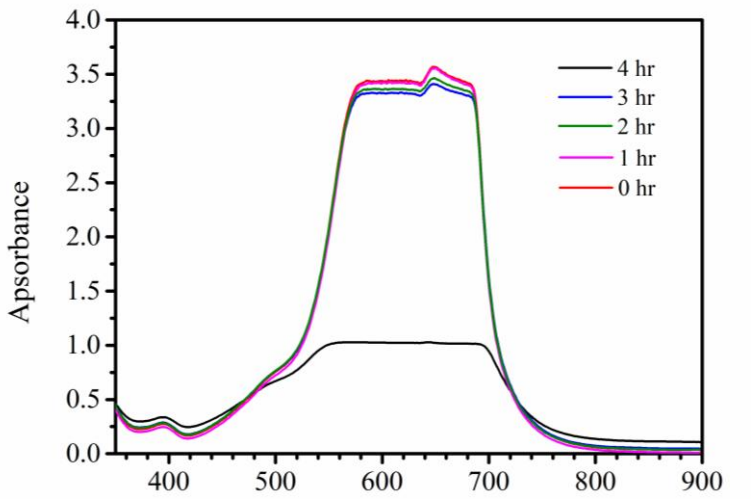
$$ZnO(e^-) + O_2 \rightarrow O_2^{\cdot} \qquad \ldots\ldots\ldots\ldots \quad 4$$

$$O_2^{\cdot} \xrightarrow{H^+} HO_2^{\cdot} \qquad \ldots\ldots\ldots\ldots \quad 5$$

$$Dye + h^+ \rightarrow oxidation\ products \qquad \ldots\ldots\ldots\ldots \quad 6$$

$Dye + e^{-} \rightarrow$ reduction $products$ 7

$Dye + OH \rightarrow$ degradation $product$ 8



Figure(7): UV–Vis spectra of MB dye under different UV illumination time

4. Conclusions

ZnO nanorods can be prepared onto glass substrates using CBD method using ZnO nanoparticles seed layer. The produced ZnO NRs have good crystallinity with hexagonal phase. The grown ZnO NRs formed as a hexagonal rods covered the whole surface of the substrate. The energy band gap was 3.27eV which closed to standard value of ZnO. Two emission peaks are appeared in the photoluminescence (PL) spectrum at a wavelength of 381nm and other one at 540nm corresponding to near band-to-band electron-hole recombination and due to oxygen vacancies, respectively. Degradation rate of MB blue dye was increased from 0.01% after 1h of illumination to 71.4% after 4h of illumination. Thus, the present results show that ZnO nanorods can be used for photocatalytic application.

Abbreviations

CBD: chemical bath deposition
FESEM: Field Emission Scanning Electron Microscope
NRs: Nanorods
CVD: chemical vapor deposition
UV: ultra violet
XRD: ray diffraction
PL: photoluminescence

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