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# Laser Enhanced Photocatalyic Degradation of Methylene blue using Nanostructured ZnO Catalyst based on Interfacial Charge Transfer

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**Abstract:** In this research, annealed nanostructured ZnO catalyst water putrefaction system was built using sun light and different wavelength lasers as stimulating light sources to enhance photocatalytic degradation activity of methylene blue (MB) dye as a model based on interfacial charges transfer. The structural, crystallite size, morphological, particle size, optical properties and degradation ability of annealed nanostructured ZnO were characterized by X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM) and UV-VIS Spectrometer, respectively. XRD results demonstrated a pure crystalline hexagonal wurtzite with crystalline size equal to 23 nm. From AFM results, the average particle size was 79.25nm. All MB samples and MB with annealed nanostructured ZnO catalyst were exposed under sunlight and lasers with (632.8,532 and 405 ) with 1.6 mW\mm2 power density irradiation for (0,30,60 and 90) minutes. UV-VIS Spectrometer was used to evaluate the photodegradiation of MB with and without annealed nanostructured ZnO catalyst where an appreciable photocatalytic generation of hydroxyl was radicals exhibited due to increasing charge separation rate and decreasing recombination rate .Nanostructured ZnO Overall results show that MB degradation achieved 66% after 90 minutes using 405nm laser irradiation, while the reaction rate constant that fits a pseudo-first order kinetics (ka) is 0.011min-1 compared to 0.0001min-1 using MB alone . This study proved that 405 nm laser and sun light are highly efficient sources to enhance interfacial charge transfer to improve photodegredation of MB dye using annealed nanostructured ZnO.

***Keywords:*** *laser, nanostructured ZnO, Photodegradiation, interfacial charge transfer*

## Introduction

Metal oxides are widely present in nature and some of them are of great practical use [1]. Zinc oxide (ZnO) is one of these oxides, which are used in many fields [2]. Zinc oxide (ZnO) has stimulated great research interest due to its unique optical and electrical properties that are useful for nanolasers [3], solar cells [4], gas sensors [5, 6], and photocatalyst [7,8]. ZnO-based photocatalytic and photoelectrocatalytic oxidation processes have an increasing attention in wastewater treatment because they are non-toxic, chemically and biologically stable materials with high photosensitivity [9]. ZnO has been extensively investigated as a semiconductor photocatalyst due to its wide direct band gap 3.1 eV.In the area of water purification, the adaptation of highly advanced nanotechnology offers the possibility of an efficient removal of chemical and biological pollutants. Dyes are presented in many foods and drugs products and have been reported as a possible cause of asthma, urticaria, and angioedema [10]. They are produced in large amounts and they enter the water stream during the production and manufacturing processes at different industrial plants. One of the most important dyes is Methylene blue (MB) which is used as a model because it is a colored substance for organic contaminant in wastewater, where it can be easily monitored by spectrophotometry measurements. It has many advantageous properties like high photostability

and water solubility. Solar energy is a clean renewable source ideal for environmental and sustainable applications; therefore it is used as a photodegradiation of MB with and without catalysts. On the other hand, laser light has unique properties like monochromaticity, high intensity, and low beam divergence. It is of great interest to use laser radiations as an excitation source to study the activity of photocatalyst. Several works were published in the photocatalytic process to enhance the efficiency of photocatalyst due to interfacial charge transfer [11-13]. The aim of this research is to engineer novel useful laser catalytic systems with nanometer dimensions as a promising friendly solution to increase sensitivity for environmental remediation using annealed nanostructured ZnO to understand more accurately the interfacial charge transfer on the catalysts surface .

**Experimental details: (Material)**

In our work, Zinc Acetate Dehydrate (ZAD) (Zn (CH3COO) 2_2H2O) and Methylene blue dye (C16H18N3SCl) were supplied from Central Drug Hose, India. The 2-methoxyethanol (C3H8O2) and monoethanolamine (MEA) (C2H7NO) were purchased from Scharlab S.L.Spain.

**Preparation of photocatalyst**

A glass substrate dipped in the chromic acid to remove organic impurities, and then soaked in soap solution to remove any grease present. These slides were then ultrasonically cleaned by distilled water for 10 min each to remove any dust or contaminants present and kept for overnight to dry. 0.45 M precursor solution was prepared by dissolving (ZAD) in 2-methoxyethanol and (MEA). which are used as solvent and stabilizer, respectively. 1:1 molar ratio mixture of ZAD to MEA. The mixture was stirred on a hot plate at 65 °C for 1 h until getting a transparent homogeneous solution. The prepared solution was spun on the pre-cleaned substrates using spin coating technique. In order to evaporate the solvent and remove the organic residuals, the films were dried for 5 min after each coating in an open air furnace at 150°C. The process was repeated several times to get the desired film thickness. The final ZnO thin film was annealed at 390°C for 3 h.

**Characterization techniques**

The characterization, structure and the average crystal size of the photocatalyst were measured using Bruker D2 phaser X-ray diffractometer with Cu kα radiation at λ=1.5418 Å. The morphology and the average particle size of the nanostructured ZnO thin film were analyzed using atomic force microscopy (AFM, modal AA 3000 scanning probe microscope from Angstrom Advanced Inc., USA). The absorbance spectra of the samples were recorded in the wavelength range 300–1000nm using a UV–VIS (SHIMADZU 1800) spectrophotometer.

**Evaluation of photocatalytic activity**

The photocatalytic experiments were conducted under ambient atmospheric conditions at natural pH using sunlight as the light source and He-Ne laser at 632.8 nm, laser diode at 532 nm and laser diode at 405 nm . All lasers have 1.6 mW\mm2 power density at 15 cm distance from solution. All ZnO samples were immersed in a quartz vessel containing the MB solution with concentration (0.019g/L).The experimental setup using sunlight and lasers light to degrade MB employing annealed nanostructured ZnO catalyst are shown in Figures (1-1) and (1-2) , respectively.

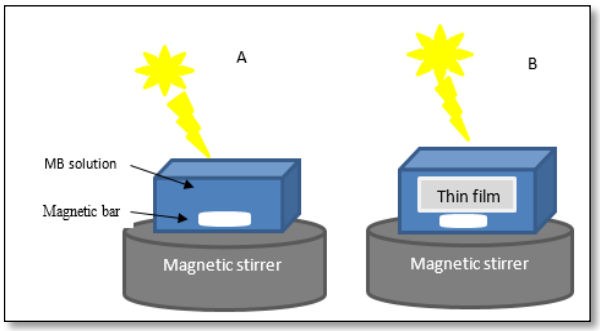


**Fig.(1):** The experimental schematic for photocatalytic degradation of MB solution under sunlight (A) MB solution without catalyst (B) MB with ZnO thin film

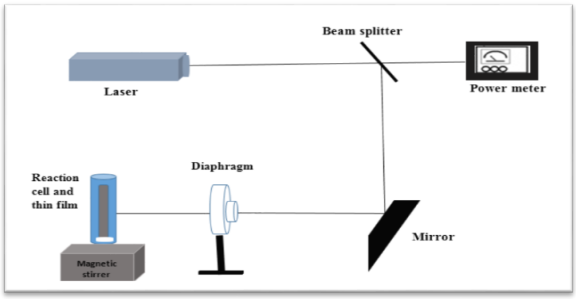


**Fig. (2):** Schematic representation the setup of the photodegradations of aqueous methylene blue using 632.8, 532,405nm wavelengths

In order to ensure adsorption/desorption equilibrium, the solution was stirred for about 45 min in dark, prior to the irradiation. The exposure times are (0, 30, 60, 90) minuets. The absorption spectra were taken after every irradiation exposure time for MB and with annealed nanostructured ZnO thin film. The degradation rate of MB dye was calculated using the following equation

The percentage degradation rate of dye (%) = $(1-C_t/C_0) \times 100\%$ ……. (1-1)

Where $C_0$ is the initial concentration and $C_t$ is the final reaction concentration

**Results and discussion**

The crystal structure of annealed nanostructured ZnO thin film was investigated by X-ray diffraction (XRD) (Figure 3).

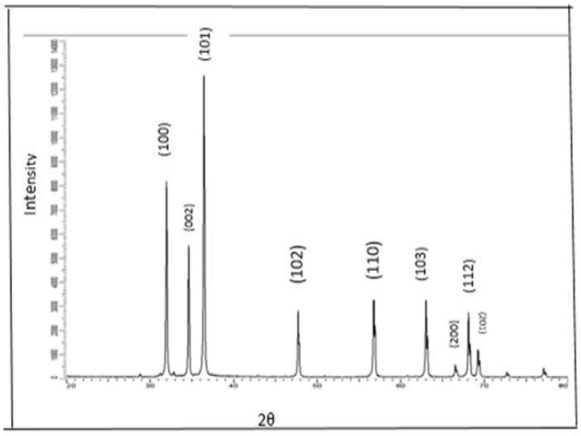


**Fig. (3):** X-Ray diffraction pattern of ZnO

The sample was indicated a crystalline hexagonal wurtzite ZnO structure with the lattice constants (a = b = 3.2299 Å and c = 5.1755 Å), which are consistent with the values in the standard card (JCPDS 36-1451). In addition, the originating sharp and intense diffraction peaks are at (100), (002), (101), (102), (110), (103), (200), (112) and (201) phase , confirmed at 2θ values equal to 31.67°, 34.31°, 36.14°, 47.40°, 56.52°, 62.73°, 66.28°, 67.91° and 69.03°, respectively. There is no evidence of bulk remnant materials and impurities. From the x-ray spectrum, the average crystalline size of nanostructured ZnO is 23 nm calculated by Debye–Scherrer equation [14].
The photocatalytic activity of the system increases dramatically with decreases crystalline size due to raised surface to volume ratio [15]. A significant fraction of the atoms (or molecules) in such systems are surface atoms that can gain surface reactions. A purity crystalline with a very little amount of defects and a weak hardness measured by dislocation density is 20.66 $\times 10^{-}4$ (nm) $^{-2}$. Therefore, it can be suggested that annealing method is an effective method to repair the structural defects of the nanostructured ZnO sample. The defects can become the recombination center of the photogenerated charges and thus can worsen the photocatalytic activity. So, the high purity of nanostructured ZnO can be improved the photocatalytic activity. The topological properties of annealed nanostructured ZnO thin film was done by AFM as in Figure (4).

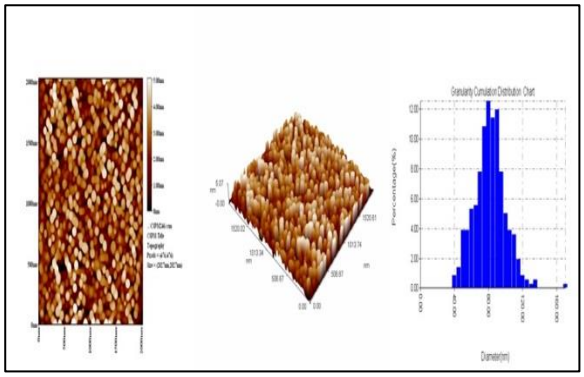

**Fig.(4):** 2D, 3D images and granularity distribution chart of the atomic force microscopy of the nanostructured ZnO thin film

The average particle size was 79.25nm and the surface roughness was equal to 1.22 nm. Figure (4 2D) shows a large number of grain size with a circle-shape and quasi-homogeneously, which indicates the crystalline nature of the films. From the AFM image (4 3D) of nanostructured ZnO, a dense nanorods can be expected growing perpendicularly and uniformly on the substrate leading to increasing the surface roughness of nanostructured ZnO thin film which enables better adsorption of MB dye on the thin film surface and increasing photocatalytic reaction. From the granularity distribution charts, the distribution of particles size was Gaussian curve in a range between 40 and 120 nm. Optical absorption spectra of the nanostructured ZnO thin films in the wavelength range of 300–1000 nm are depicted in Figure (5).

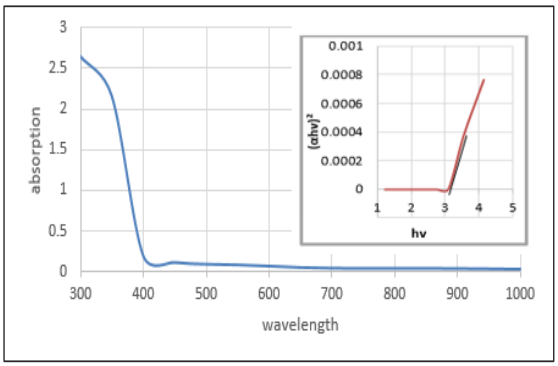


**Fig. (5):** The absorption spectrum and optical band gap of nanostructured ZnO thin film

As shown, the absorption intensity of the nanostructured ZnO thin film in the UV region with wide optical band gap energy Eg is 3.2 eV which leads to high photocatalytic activity. The optical band gap of micro- and nano-crystals of ZnO is approximately similar with a slight shifting. Also the variation in optical band gap is according to the manufacturing methods [16-18].Nevertheless, narrow band gap semiconductors is difficult to maintain photoactivity over a long period of time due to the fast recombination of photogenerated electron–hole pairs. Notably, the band gap depends on the crystalline structure and the defects in the network of nanostructured ZnO. Figure (6) shows the comparative relation between sunlight and different lasers irradiation to degrade MB for different exposure times.

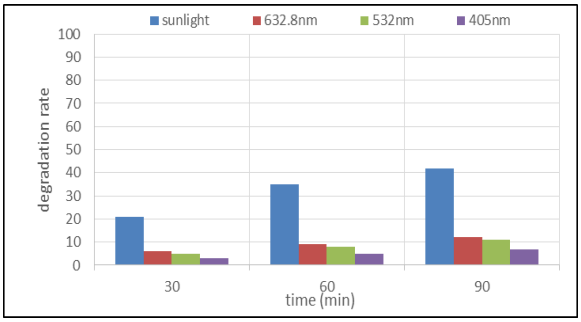


**Fig. (6):** Comparison of the degradation rates of MB dye without catalyst under sunlight and three different lasers wavelengths

Hence, the remarkable change in absorption spectra can be observed and the blue color of Methylene Blue solution was gradually changed to transparent color with increasing exposure time. Furthermore, photodegradation rate increased directly with increasing exposure times. Also the photodegradation rate by sunlight is highest than that by lasers because of its broadband region. The degradation rate of MB in 405 nm is lower than 632.8 nm and 532 nm because MB has low absorbance with this wavelength as shown in Figure (7). After addition of nanostructured ZnO catalysts to the solution, the photodegradiation rate was increased as shown in Figure (8). The photodegradation rate with nanostructured ZnO under sunlight and lasers wavelength are higher than MB alone. In this Figure, a second more efficient source is 405 nm and it can be expected to be the first one at time larger than 90min. The photodegradation rate at sunlight and 405 nm laser are largely increased than other lasers because the poton energy approximately equal the band gap of the nanostructured ZnO catalyst.

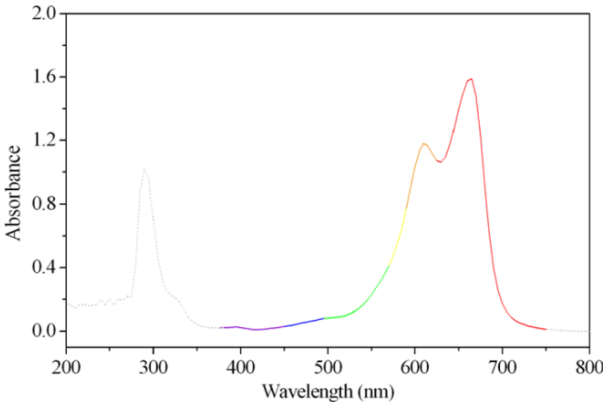


**Fig. (7):** The absorption spectrum of Methylene Blue (MB)

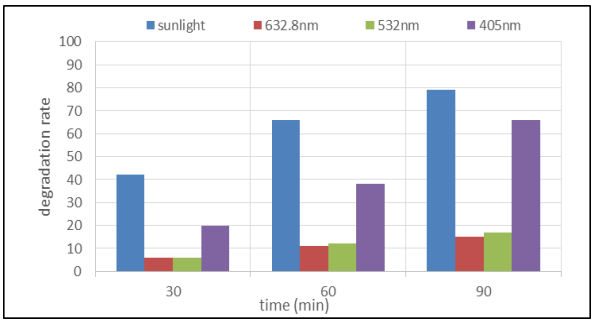


**Fig. (8):** Comparison of the degradation rates of MB dye with nanostructured ZnO catalyst under sunlight and three different lasers wavelengths.

The pseudo-first order kinetics (ka) fitted to the rate of removal of MB (or the reaction rate) [19] depended on change in concentration of MB under sunlight and (632.8, 532,405) nm laser irradiation for various exposure times. The values of rate constant for two reaction systems are in Table (1-1). The photocatalyst activity mechanism of the nanostructured ZnO catalyst can be described sequentially starting from

Equation (1-2) to Equation (1-8). Nanostructured ZnO irradiated with a photon energy (hυ) approximately matches or exceeds its band gap energy (Eg). Electron-hole pairs were generated. The electrons can be excited from the valence band (VB) to the conduction band (CB), leaving the same number of holes behind in the VB. Holes can react with water adsorbed molecules to form highly reactive hydroxyl radicals (OH•) as in Equation (1-3). Meanwhile, on the surface of the thin films, oxygen is trapping the CB-electron to produce superoxide radical (O•2) as in Equation (1-4). The formed radicals in redox process have a powerful oxidation ability to degrade MB organic dye to produce CO2 and H2O as in Equation (1-8). This step involves interfacial charges transfer between the surface of the nanostructured ZnO photocatalyst and the adsorbed MB

$$ZnO + h\upsilon \rightarrow e_{CB} + h_{VB} \quad (1)$$

$$H_2O + h_{VB} \rightarrow OH\bullet + H^+ \quad (2)$$

$$O_2 + e^- \rightarrow (O\bullet^-_2) \quad (3)$$

$$O\bullet^-_2 + H^+ \rightarrow HO\bullet_2 \quad (4)$$

$$2HO\bullet_2 \rightarrow H_2O_2 + O_2 \quad (5)$$

$$H_2O_2 + O\bullet^-_2 \rightarrow OH\bullet + O_2 + OH^- \quad (6)$$

$$OH\bullet + \text{MB organic dye} \rightarrow CO_2 + H_2O \quad (7)$$

**Table (1):** The rate constants of MB solution without catalyst and with nanostructured ZnO catalyst.

| | The pseudo-first order kinetics $[K(min)^{-1}]$ Under sunlight | The pseudo-first order kinetics $[K(min)^{-1}]$ Under 632.8nm | The pseudo-first order kinetics $[K(min)^{-1}]$ Under 532 nm | The pseudo-first order kinetics $[K(min)^{-1}]$ Under 405 nm |
|---|---|---|---|---|
| MB | 0.018 | 0.0004 | 0.0003 | 0.0001 |
| MB with nanostructured ZnO | 0.031 | 0.0006 | 0.0035 | 0.011 |

## Conclusions

Novel friendly environmentally nanostructured ZnO catalyst system was successfully accomplished. Nanostructured ZnO photocatalytic is more efficient than direct photolysis. This study clearly demonstrates that sunlight and 405 nm diode laser with 1.6 mW/mm2 power density induced photocatalytic degradation using nanostructured ZnO could be used as an efficient method as compared with other sources and could be applied effectively to purify wastewater.

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## الليزر المعزز للانحلال التحفيزي للمثيلين الأزرق المبني على أساس انتقال الشحنات السطحية باستخدام المحفز أوكسيد الزنك النانوي الملدن

**هبة كاظم وهاب  زينب فاضل مهدي  رواء احمد فارس  داود عبيد الطيفي**

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**الخلاصة:** في هذا البحث، تم تصنيع جهاز نانوي لتصفية المياه باستخدام اوكسيد الزنك بالابعاد النانوية الملدن كعامل مساعد محفز واستخدام ضوء الشمس وليزرات مختلفة الاطوال الموجية كمصادر ضوئية محفزة لتعزيز فعالية التفكك الضوئي لصبغة الميثلين الزرقاء المستخدمة كموديل المبني على اساس انتقال الشحنات االسطحية. تم فحص التركيب ،حجم البلورة ،التشكيل ،حجم الحبيبة ،الخواص البصريه وقابلية التفكيك لاوكسيد الزنك الملدن باستخدام جهاز حيود الاشعه السينيه ، مجهر القوة الذري ومطياف الاشعه الفوق البنفسجيه - المرئيه. نتائج الاشعة السينية بينت التركيب البلوري النقي السداسي لمادة اوكسيد الزنك وبلورته بحجم 23 نانومتر بينما نتائج مجهر القوة الذري اظهر معدل حجم الحبيبه ب 79.25 نانومتر . تم تعريض الصبغة الزرقاء لوحدها والصبغه الزرقاء مع اوكسيد الزنك النانوي الملدن لاشعة الشمس واشعة الليزرات بالاطوال موجية (632.8,532,405) نانومتر وبكثافة قدرة 1.6ملي واط/ملم2 وبفترات تعريض (30,60,90) دقيقة. استخدم مطياف الاشعه الفوق البنفسجيه - المرئيه لقياس فعالية التفكك الضوئي لصبغة الميثلين الزرقاء مع وبدون اوكسيد الزنك النانوي من خلال زيادة توليد الجذور OH• نتيجة زيادة معدل انفصال الشحنات وتقليل معدل اعادة الاتحاد. النتائج اوضحت ان تفكك صبغة المثيلين الزرقاء بوجود اوكسيد الزنك في 90 دقيقه وصل الى 66% باستخدام ليزر 405 نانومتر اما معدل التفاعل فوصل الى (0.011) في الدقيقة مقارنه ب(0.0001) في الدقيقة للصبغه الزرقاء وحدها . من هذه الدراسه، يمكن الاستنتاج بان ليزرالدايود 405 نانومتر بالاضافة للشمس كفؤ جدا لتعزيز انتقال الشحنات السطحية لتحسين فعالية التفكك لصبغة المثيلين الزرقاء باستخدام اوكسيد الزنك الملدن النانوي .