CZECH TECHNICAL UNIVERSITY IN PRAGUE

FACULTY OF ELECTRICAL ENGINEERING

BACHELOR THESIS

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Rubin Hao

CZECH TECHNICAL UNIVERSITY IN PRAGUE

Faculty of Electrical Engineering

Department of Physics

Bachelor Thesis:

Photocatalytic degradation of organic pollutants

Project of:	Rubin Hao
Supervisor:	David Rutherford Ph.D.
Study program:	Electrical Engineering and Computer Science

Prague 2023

BACHELOR'S THESIS ASSIGNMENT

I. Personal and study details

Student's name: **Hao Rubin** Personal ID number: **472491**

Faculty / Institute: **Faculty of Electrical Engineering**

Department / Institute: **Department of Electrical Power Engineering**

Study program: **Electrical Engineering and Computer Science**

II. Bachelor's thesis details

Bachelor's thesis title in English:

Photocatalytic degradation of organic pollutants

Bachelor's thesis title in Czech:

Fotokatalytická degradace organických polutantů

Guidelines:

This experimental project will investigate the ability of different types of nanoparticles to degrade organic pollutants under different light sources. Degradation of organic pollutants will be monitored by real-time UV-vis spectroscopy in absorbance mode. This technique creates inactivation curves (ie changes in absorbance over time) from which reaction rates can be calculated. When photosensitive nanoparticles in a liquid are illuminated with sufficient energy, reactive oxygen species (ROS) will be generated, which are thought to be responsible for the degradation of organic pollutants. To investigate this, ROS measurements will also be performed along with measurements of organic pollutant degradation. After completing the project, the student will gain knowledge about the basic mechanisms of photocatalytic degradation of organic pollutants.

Bibliography / sources:

Cambrussi et al., Matéria (Rio J.) 24 (4) • 2019 (https://doi.org/10.1590/S1517-707620190004.0807)

Name and workplace of bachelor's thesis supervisor:

David Rutherford, Ph.D. Department of Physics FEE

Name and workplace of second bachelor's thesis supervisor or consultant:

Date of bachelor's thesis assignment: **15.07.2022** Deadline for bachelor thesis submission: **10.01.2023**

Assignment valid until: **09.01.2024**

David Rutherford, Ph.D. Supervisor's signature	doc. Ing. Zdeněk Müller, Ph.D. Head of department's signature	prof. Mgr. Petr Páta, Ph.D. Dean's signature

III. Assignment receipt

The student acknowledges that the bachelor's thesis is an individual work. The student must produce his thesis without the assistance of others, with the exception of provided consultations. Within the bachelor's thesis, the author must state the names of consultants and include a list of references.

Date of assignment receipt	Student's signature

Declaration:

I declare that the presented work was developed independently and that I have listed all sources of information used within it in accordance with the methodical instructions for observing the ethical principles in the preparation of university theses.

Prague, date ....

Author’s signature

Acknowledgment:

First and foremost I am extremely grateful to my supervisor, David Rutherford, Ph.D. for his invaluable advice and patience. His positive attitude gave me great encouragement during my experiments and writing process. At the same time, I would also like to thank my classmates for sharing their experiences with me selflessly while writing. Finally, I would also like to thank my parents. It was their support that allowed me to complete the research of the thesis without any worries.

Abstract

Nowadays, residual dyes from different sources have become an important issue of water pollution, and a wide variety of persistent organic pollutants have been introduced into our natural water resources without wastewater treatment systems. This widespread problem of water pollution is jeopardizing our health. Therefore, it is essential to remove these organic pollutants before discharge into the environment. Various techniques have been employed to degrade these organic pollutants and photocatalysts involving zinc oxide appears to be one of the most promising techniques. In recent years, zinc oxide nanoparticles use as photocatalysts have attracted much attention due to their extraordinary properties such as large area surface structure.

In this paper, we focus on the photocatalytic efficiency of gallium-doped zinc oxide nanoparticles using a representative organic pollutant, methylene blue. In the experimental study, the excitation light source used for the photocatalyst was an illumination device within visible spectrum (i.e. 400-700 nm). The experimental results showed that the concentration of organic pollutant was reduced by about 20% after only 180 minutes. The feasibility of visible light as an excitation source for gallium-doped zinc oxide nanoparticles was also determined by a controlled variable approach.

The result that the photocatalytic process can be carried out in visible light is encouraging. On the one hand, the visible light is much more radiant than the ultraviolet light in the sunlight that hits the surface after passing through the atmosphere. On the other hand, this makes it much more practical for indoor use. In summary, this experimental study is of great importance in terms of convenience, economy and safety of photocatalyst development.

Key Words: Zinc Oxide nanoparticles, Methylene Blue, Gallium doped Zinc Oxide, organic pollutant, photocatalytic degradation

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List of Abbreviations

ZnO	Zinc Oxide
GZO	Gallium doped nano Zinc Oxide Nanocrystals
MB	Methylene Blue
nZnO	Nano Zinc Oxide
AOPs	Advanced oxidation processes

Figures

Introduction

Water resources are the source of life, 70% of the earth's surface is covered by water, however 97.5% of which is sea water which is undrinkable for humans and unusable for industry. Even so, a large part of freshwater resources are unusable resources (such as glaciers, deep groundwater, etc.). Therefore, the fresh water resources we can use are very limited. With the continuous increase of water consumption in industry, agriculture and cities, more and more polluted water resources need to be treated. [1]

With people's emphasis on solar energy, the research and development in the field of photocatalysis has also made great progress. One of the major applications of this technology is the degradation of organic pollutants in water and air streams which is considered as one of the so-called advanced oxidation processes (AOPs). [2]

AOPs are a group of chemical treatment processes designed to remove organic matter from wastewater by oxidation in reaction with hydroxyl radicals (-OH). These reactive substances are the most powerful oxidizing agents and once the hydroxyl radicals are formed they react non-selectively and the pollutants will be quickly and efficiently broken up and converted into small inorganic molecules or even mineralized substances. [36]

1.1 Zinc Oxide

ZnO is an inorganic compound that is white powder at room temperature and insoluble in water. It is also widely used in industry, commerce, food industry and many other fields. Although zinc ore is discovered under natural conditions, most ZnO is synthesized in laboratories.[6] ZnO is an environmentally friendly material in low concentration. because it is compatible with organisms, making it ideal for a wide range of daily applications without any risk to human health and environmental impact. The U.S. Food and Drug Administration (FDA) also lists ZnO as one of the safest metal oxides for use in the food industry. [10]

1.1.1 Properties of ZnO

ZnO is an n-type semiconductor having wide band gap with distinctive applications for the fabrication of light emitting diodes, photovoltaic devices, gas sensors, piezoelectric devices and for photocatalysis etc. [3]. The optical and magnetic properties of ZnO can be changed or improved by using nanoscale ZnO. [4] Miniaturized zinc oxide has a higher surface-to-volume ratio compared to the bulk, which means higher reactivity in photocatalysis.

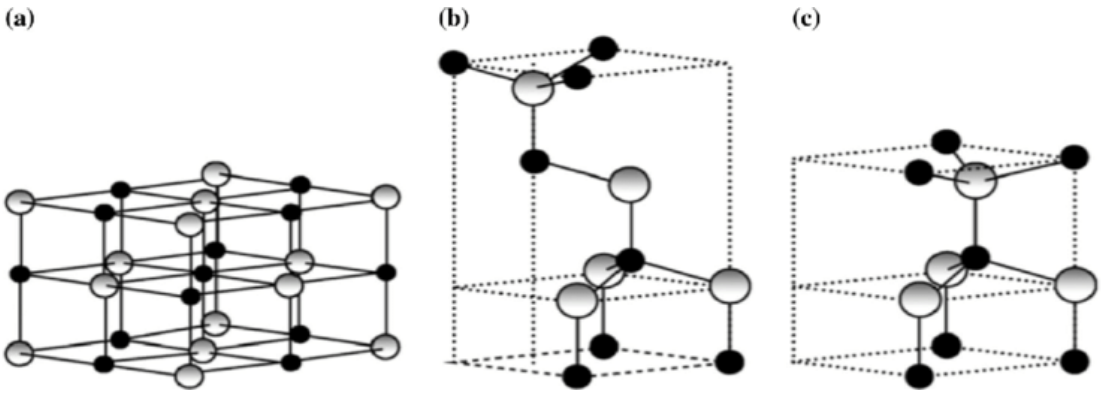


Fig.1.1 different network structures of ZnO nanoparticles (a)cubic rocksalt, (b)cubic zincblende, (c) hexagonal-wurtzite [7]

The shaded grey and black spheres shown in Fig.1.1 represent Zn and O atoms, respectively.

(a) – The zincblende structure will be stable by growing on cubic substrates.

(b) – The rocksalt structure will be stable by growing on cubic substrates at relatively high pressures of 10GPa. [9]

(c) – The wurtzite structure is most common and stable at ambient conditions due to its ionicity that lies between the covalent and ionic materials.[8]

ZnO have received extensive attention in the degradation of environmental pollutants. The greatest advantage over certain semiconducting metal oxides is its ability to absorb a wide range of solar spectrum and a great number of photons. The main disadvantages of ZnO are wide bandgap energy and photo-corrosion. Due to its broadband energy, the light absorption of ZnO is very limited in the visible region. This leads to rapid recombination of photogenerated charges, resulting in low photocatalytic efficiency.[5]

Property	Value
Energy band-gap (E_g)	3.2–3.7 eV (Direct)
Exciton binding energy	60 meV
Effective electron mass (M^*)	0.24–0.30 m_e
Effective hole mass (m_h^*)	0.45–0.60 m_e
Electron Hall mobility at 300 K for n-type (μ_e)	200 $cm^2\ V^{-1}\ S^{-1}$
Electron Hall mobility at 300 K for p-type	5–50 $cm^2\ V^{-1}\ S^{-1}$
Refractive index (nw, ne)	2.008, 2.029
Intrinsic carrier concentration (n)	$<10^6\ cm^{-3}$
Background carrier doping	n-type: $\approx 10^{20}$ electron cm^{-3} p-type: 10^{19} holes cm^{-3}
Optical transmission, T ($1/\alpha$)	80–95%

Fig.1.2 optical and electrical properties of single crystal wurzite [7]

ZnO nanoparticles have several advantages, including chemical and thermal stability, robustness, and a long shelf life than other metal oxides. In such case, ZnO has been chosen used in high-power electronic devices (field emission devices etc.) due to its excellent electrical properties.[31]

The authors of the article [25,26] show the UV-visible absorption spectrum and reflectance spectrum of ZnO nanoparticles. The maximum absorbance of ZnO nanoparticles appears around the wavelength of 367 nm (which may vary depending on the synthesis method), which is in the UV region. In the visible wavelength range, the absorbance of ZnO nanoparticles decreases rapidly and the reflectance reaches 90%. At wavelengths of 400-450 nm, where absorbance and reflectance change rapidly, light sources operating in this range need to be explored as possible illumination sources.

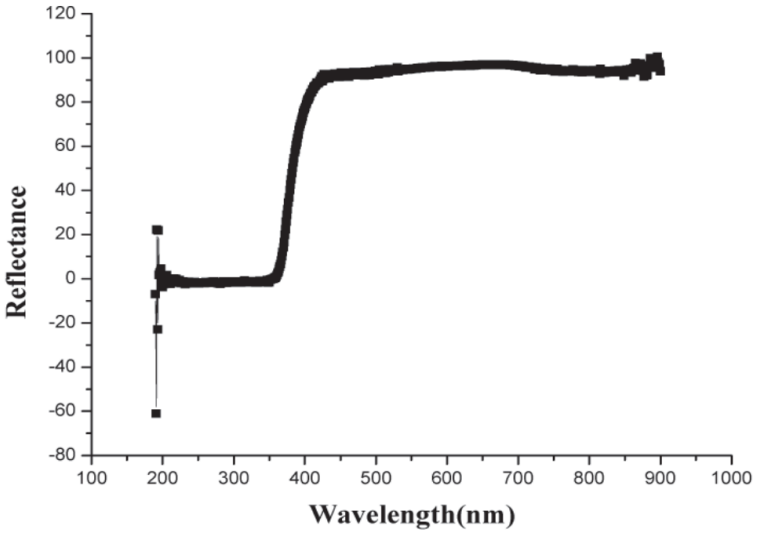


Fig.1.3 Reflectance spectrum of ZnO nanoparticles [26]

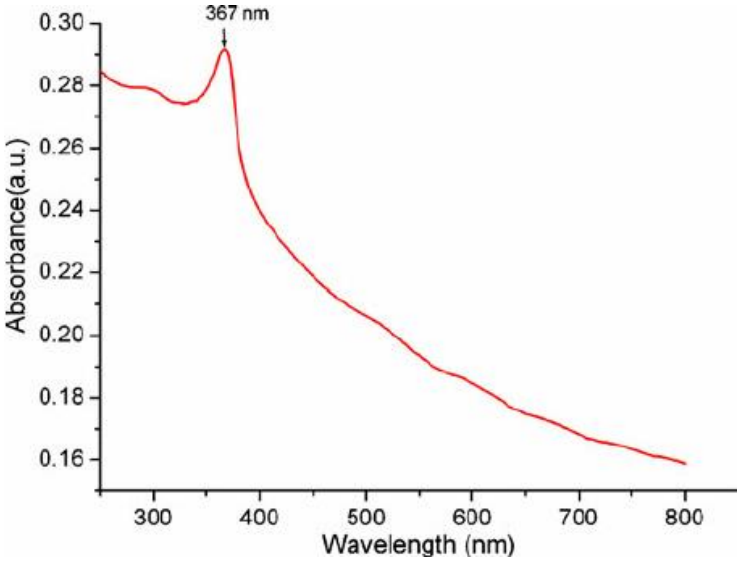


Fig.1.4 UV–visible absorption spectrum of the ZnO nanoparticles. [25]

Doping, coupling, and morphology modification of metal oxide material are well-known methods to improve light absorption in the visible region. The optical properties, structure and electrical properties of ZnO can be modified by doping with element of group III, such as aluminum (Al), gallium (Ga) and indium (In). These elements are characterized by having three valence electrons and the ability to form shared pairs with ZnO. Moreover, it has been shown that the doping of these elements can increase the effectiveness of the photocatalytic ability of ZnO compounds. [32] The effect of synthesis on the material will be discussed in the next subsection.

1.1.2 Synthesis of ZnO nano particles

As mentioned earlier, most ZnO comes from laboratories and nanomaterial can be synthesized by 4 different ways: physical, chemical, biological and hybrid method of synthesis.

In the physical methods, the idea is by breaking down bulk matter over and over again until nanoscale dimensions are reached, a process called top-down approach. Specific examples as laser ablation, in which atoms are removed from the solid by a thermal or nonthermal process with an intense laser beam; physical vapor deposition, in which material as vapor particles are transferred from source material to the substrate and so on. [11]

In the chemical method, nanomaterials are produced by ‘grow up’ method. Atoms, molecules or ions in solution form nucleation first and then aggregate these species to finally become nano-sized particles, a process called bottom-up approach. The process of combining the precursor chemicals is typically under wet chemistry and adjusting reaction parameters can control the shape and size of the synthesized nanoparticle. This is the most widely used method for the production of nanomaterials in industry for reasons of synthetic convenience. [12] There are many methods categorized under this approach like solvothermal, microwave irradiation, pyrolysis etc.

In the biological method, microorganisms or extracts of plants along with a precursor are used to form the desired nanomaterials. Biological methods of producing nanomaterials from plant extracts have more advantages than the usual chemical methods, because the progress can be more quickly with low cost of precursors and energy expenditure while ensuring high purity product with simpler synthesis procedure and lab equipment. The disadvantage of biosynthesis method by using extracts of plants is that is more difficult to control particle size and shape compared with chemical methods. [13]

The hybrid method include: Biohydrothermal, Electrochemical, Chemical Vapor Deposition etc.

There are several factors influencing the synthesis of ZnO nanoparticles are mentioned:

1. pH of reaction mixture – it determines the type of ZnO nanoparticles formed. The pH of solution will change the charge of the molecule and this change affects the reduction of the molecule. While the crystallite size, morphology, phase and surface area of ZnO nanoparticles are largely dependent on the number of positive (H+) and negative (OH-)ions. [16]
2. Calcination temperature – by heat-treating a material the particles fuse and enlarge its primary crystallite size. The process is called particle coarsening and it usually used for growth of large crystals from small size by combining smaller particles. This process could also occur at room temperature, but can be accelerated by heating. In general, it was found that the crystallite size of ZnO nanoparticles had larger size at the same time with higher calcination temperature, their purity and morphology were also affected. [15]
3. Effect of different zinc salts precursor – it influenced the morphological, textural and optical properties of ZnO nanoparticles. [17] Additionally, the crystallite size of ZnO nanoparticles increased along with the concentration of the zinc salt precursors increase.[14]
4. Reaction time – is the time required to complete all steps in the nanoparticle synthesis process, including reduction and formation. Longer reaction times give nanoparticles the opportunity to form larger particle sizes.

According to the experimental results listed in the article and the authors' analysis [14], the surface area of ZnO nanoparticles is also influenced by some of these factors. In order to obtain a larger surface area for better photocatalysis: the stirring rate and concentration of zinc precursor should be increased, the reaction temperature and calcination temperature should be reduced, it's easier to obtain a larger surface are in alkaline reflective mixtures. The aim of increasing the surface area is to obtain better photocatalytic efficiency for the degradation of pollutants.

1.1.3 Photocatalysis

The photocatalysis combines photochemistry and catalysis, which can be defined as 'the acceleration of a photoreaction in the presence of catalyst' [33]. According to phase of catalyst and reactant, there are two types of photocatalysis:

1) Homogeneous photocatalysis – the reactants and photocatalyst exist in the same phase. There are liquid phase and gas phase homogeneous catalysis. Homogeneous catalysts have relatively homogeneous active centers, high selectivity with few side reactions. However, homogeneous catalysts have the disadvantage of being difficult to separate, recover and regenerate. [18]
2) Heterogeneous photocatalysis – the catalytic reactions occur at the interface of two phases (solid-liquid, solid-gas, liquid-gas), most of the catalytic reactions used in industry belong to heterogeneous photocatalysis. Heterogeneous photocatalysis occurs on the surface of the catalyst, the reactions involves the process of diffusion of reactant molecules within the catalyst pores, absorption on the surface, reaction on the surface, and desorption and intra-pore diffusion of product molecules. [19]

In most cases, the heterogeneous photocatalyst refers semiconductor photocatalyst, and the catalyst is mostly in solid phase (e.g. nanoparticle), while the reactant is in the liquid phase or gas phase. Importantly, the heterogeneous photocatalysis process occurs only at specific sites on the catalyst surface and these sites are called active sites. But the surface area of a solid catalyst still has strong influence on the number of available active area. [20]

The principle of photocatalysis is to use light to excite compound semiconductors such as zinc oxide. When light with energy greater than or equal to the energy gap is irradiated onto a semiconductor nanoparticle, the electrons in its valence band will be excited to leap to the conduction band, leaving relatively stable holes in the valence band, thus forming electron-hole pairs to participate in oxidation-reduction reactions (see Fig. 1.5). [21]

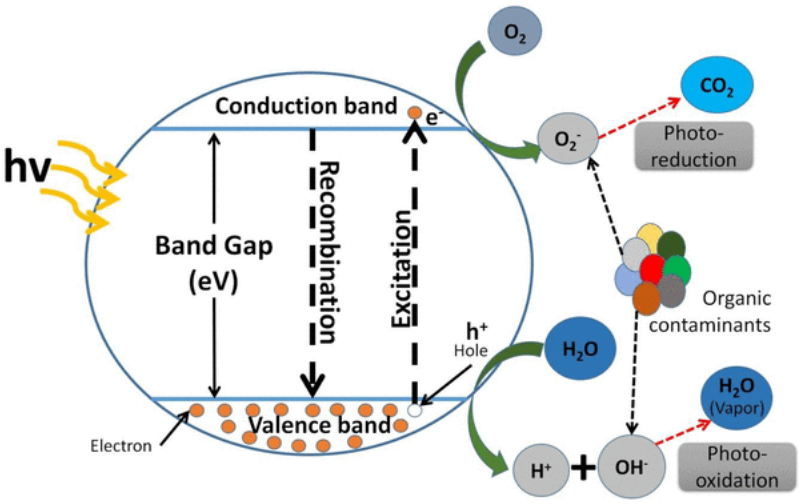


Fig. 1.5 General mechanism of the photocatalysis [29]

The goal of photocatalytic process is to mineralize the organic pollutants into carbon dioxide, water and mineral acids in the presence of ZnO particle and reactive oxidizing species, such as oxygen or air. The photocatalytic reaction starts when the ZnO particles absorb photons with energy equal or greater than their band gap energy from the illumination. In this way, light-induced electrons are lifted from the valence band (VB) to the conduction band (CB). Due to generation of positively charged holes and negatively charged electrons, oxidation-reduction reaction takes place at the surface of semiconductor. (Eq.1) [21] In addition, the positive holes generated by the light in the valence band will recombine with the electrons excited by the light in the conduction band and dissipate in the form heat. (Eq.2)

$$ZnO + hv \rightarrow ZnO\,(e_{CB}^{-} + h_{VB}^{+}) \quad (1)$$

$$e_{CB}^{-} + h_{VB}^{+} \rightarrow heat \quad (2)$$

$$h_{VB}^{+} + H_2O \rightarrow H_{VB}^{+} + \cdot OH \quad (3)$$

$$2h_{VB}^{+} + 2H_2O \rightarrow 2H_{VB}^{+} + H_2O_2 \quad (4)$$

$$H_2O_2 \rightarrow 2 \cdot OH \quad (5)$$

$$e_{CB}^{-} + O_2 \rightarrow \cdot O_2^{-} \quad (6)$$

$$\cdot O_2^{-} + H_2O + H_{VB}^{+} \rightarrow H_2O_2 + O_2 \quad (7)$$

$$H_2O_2 \rightarrow 2 \cdot OH \quad (8)$$

In oxidation reaction, the positive holes react with the moisture present on the surface and produce hydroxyl radical. (Eq.3-5) In reductive reaction, the electrons react with the oxygen molecule while forming the superoxide radicals. (Eq.6) According to the listed equations, the end products of both reactions are hydroxyl radicals. (Eq.5,8) The hydroxyl radical is oxidative in nature and nonselective which leads to the partial or complete mineralization of organic compounds. [22] Theoretically, organic pollutants should be transformed into carbon dioxide, water and other degradation products at the end by the combined action of hydroxyl radicals and superoxide.

1.2 Methylene Blue

Methylene Blue (MB) is an aromatic heterocyclic basic dye. The formula of MB is $C_{16}H_{18}ClN_3S$. It is a solid, odorless, dark green powder at room temperature and yields a blue solution when dissolved in water. MB has a characteristic deep blue color in the oxidized state and is colorless in the reduced form. [23]

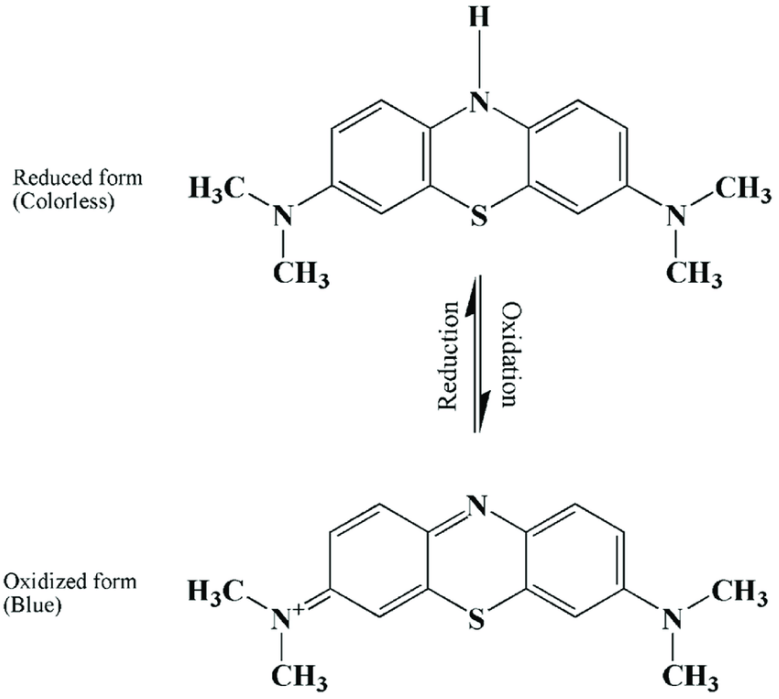


Fig.1.6 The structure of MB [30]

MB was the first synthetic antimalarial used during the late 19th and the early 20th centuries against all types of malaria. Nowadays, MB is an organic dye extensively used in the dye, textile, and plastic industries. However, this becomes a problem to humans and microorganisms with the increasing effluent discharge from the textile industry. MB is toxic, carcinogenic and non-biodegradable, posing a serious threat not only to human health but also to the environment. MB poses many kinds of risks to human health, such as respiratory distress, blindness, mental disturbances, nausea, diarrhea, vomiting, cyanosis, and shock, among others. Skin contact with MB may cause skin redness and pruritus. The release of methyl bromide into the environment is also a major threat. In addition to being a toxic supply to the food chain of organisms, it also reduces sunlight transmission and oxygen solubility, affecting the photosynthetic activity of aquatic organisms. [24]

Experimental

2.1 Sample preparation

The MB solutions used in the experiments were obtained from commercially available MB powder with the CAS code is 122965-43-9 (Sigma Aldrich). In order to find the maximum absorbance point, a total of 7 groups of equal halves were made from 10 ug/mL downwards, and an additional group of pure water solution was added as a control group. The gallium doped zinc oxide (GZO) are used as photocatalyst, it is made by Julia Micova, Ga:ZnO (10%). Seeding solution with a concentration of 2mg/mL was prepared by GZO.

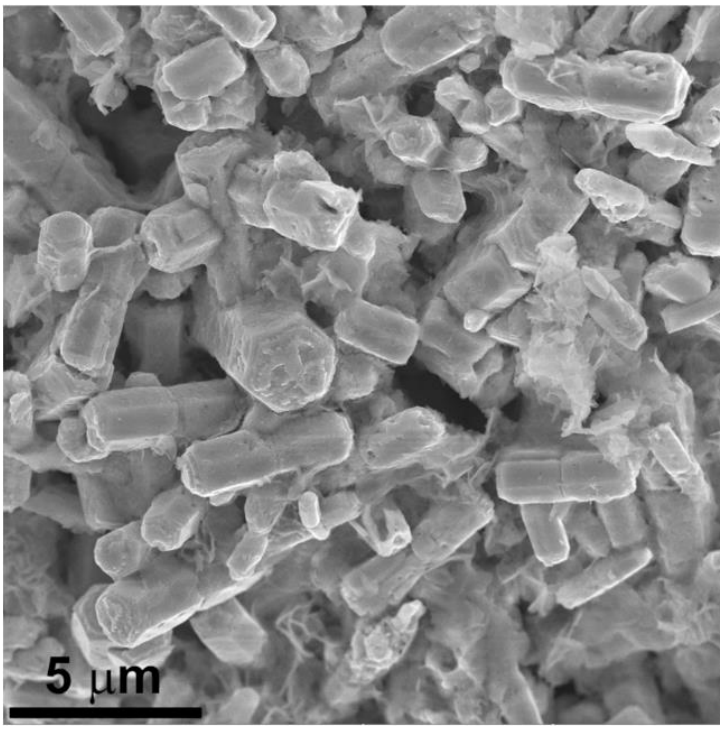


Fig.2.1The top-view SEM image of as-grown GZO NRs with magnifi-cation 10 000x. [27]

The crystal size and morphology of as-grown GZO NRs were revealed by scanning electron microscopy (SEM) (seeFigure 2.1). The top view shows hexagonal NRs with length varying from 3 to 5μm and diameter about 1μm. [27]

To verify the photocatalytic degradation ability of GZO, the experimental subjects were divided into four groups according to the involvement of GZO particles and light sources.

ZL - The MB solution was spiked with GZO and stirred continuously under the light source.

ZD - The MB solution was spiked with GZO and stirred continuously in the dark.

WL - Stirring of MB solution only under light

WD - MB solution only stirred in the dark

Fig. 2.2 A) Commercial MB B) Experimental samples

2.2 Bioreactor and light source

RTS-1C is personal bioreactor which utilizes patented Reverse-Spin® technology that applies non-invasive, mechanically driven, low energy consumption, innovative type of agitation resulting in highly efficient mixing. The excitation light source for GZO is visible light with a wavelength from 400-700 nm by KL2500LED.

The mode of the bioreactor in the experiment was 2000 rpm with 1 second reverse rotation interval. The length of the experiment was 3 hours, and samples were taken at 60-minute intervals to measure the change in absorbance of the solution.

Fig. 2.3 RTS – 1C bioreactor

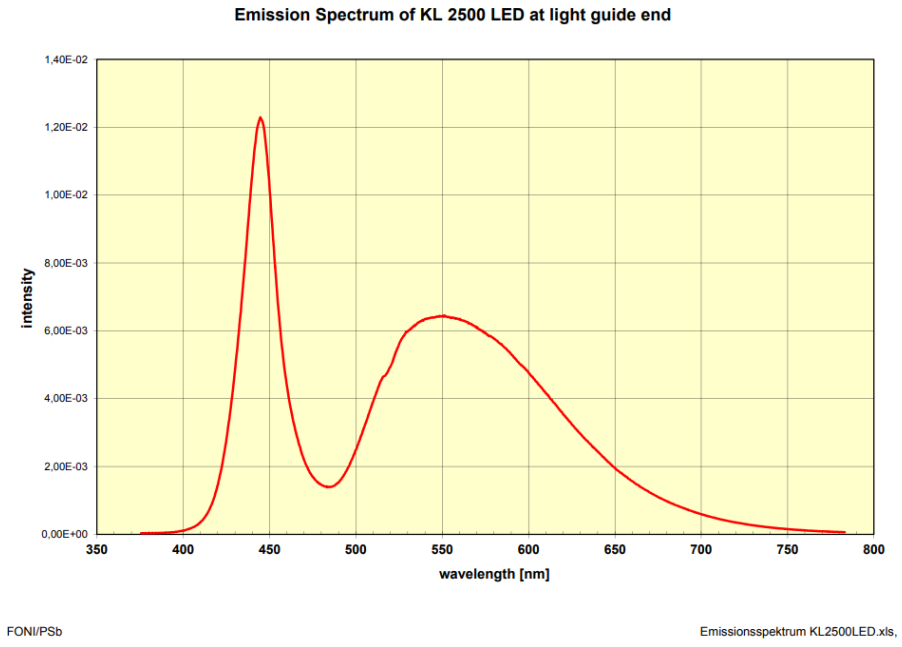


Fig. 2.4 Emission Spectrum of KL 2500 LED [34]

2.3 Spectrophotometer

The spectrophotometer is a device that measures the absorbance of wavelengths of solutions, as well as the transparency or transmittance of solids. Spectrophotometry is applied using a spectrophotometer. They can also measure the reflectance of solutions. Using different calibrations and controls, they can measure the diffusivity of light ranges in the electromagnetic spectrum covering 200 nm to 2500 nm. There are two main components of a spectrophotometer:

Spectrometer: A spectrometer uses a lens to send a straight beam of light to a prism, which divides it into individual wavelengths. A wavelength selector then filters out only the specified wavelengths and sends them to the photometer.

Photometer: The photometer detects the number of absorbed photons and sends this measurement to a digital display.

The basic principle of the spectrophotometer is based on the absorption of photons. Higher amounts of photons correspond to higher intensity of light. When we talk about the spectrum of light, we are talking about the spectrum of energy, and different levels of energy create the different colors that we perceive. Spectrophotometer is basically a calibrated light counter.

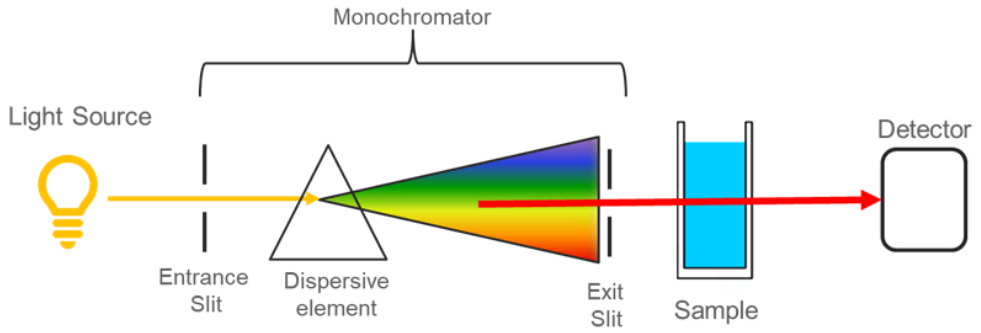
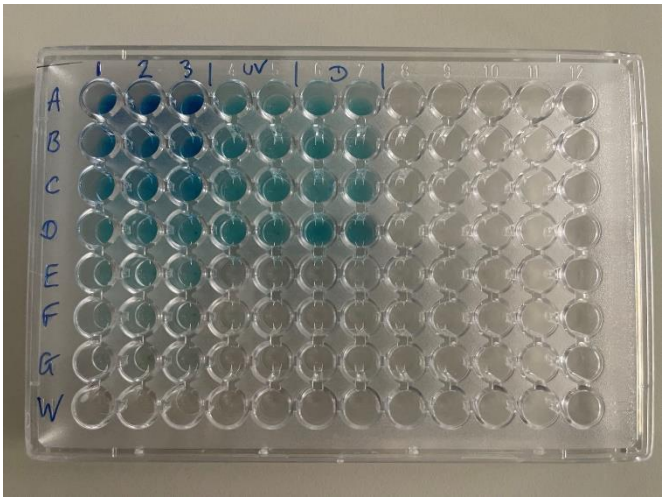


Fig. 2.5 working principle of spectrophotometer [28]

The operation and setup of the device is done in software in the computer. To ensure that the solution in the well plate is uniformly displayed, the shake mode is double orbital for 10 seconds at frequency 282 cpm (cycles per minute). spectrum range is 300-800 nm and step is 10 nm. The output is the optical density of each step in each well.

A)



B)

Fig. 2.6 A)96 well plate B) Epoch Microplate Spectrophotometer

2.4 Centrifuge

Centrifuge with cooling function MPW-150R is a high performance laboratory micro cooler. It is widely used in medical, scientific and industrial, biochemical and other types of laboratories. The powerful centrifugal force generated by the high speed rotation of the centrifuge rotor forces the particles to overcome their suspension and produce a settling motion before they are placed in the spectrophotometer, making the sample tested a pure liquid. Each sample is placed for 10 minutes at a speed of 13,000 revolutions per minute. The purpose of using a centrifuge is to eliminate the effect of (insoluble) zinc oxide on the absorbance measurement of MB.

Fig. 2.7 centrifuge MPW-150R

2.5 Summary experimental procedure

1） 7 different concentrations of MB solutions were made by equiproportional dilution and measured using a spectrophotometer to find the maximum absorbance of MB.

2） 4 MB solutions containing the same concentration were dispensed with the light source and GZO as variables. 30 minutes of pretreatment without light source stirring prior to photocatalytic experiments.

3） The same amount of solution was removed from each of the 4 samples at 0, 60, 120, and 180 minutes of the experiment.

4） Samples containing GZO were processed in a centrifuge for 10 minutes and then the absorbance change was measured by spectrophotometer together with other samples.

Results and analysis

3.1 Spectrum of methylene blue

The wavelength of maximum absorbance, also known as the maximum absorption wavelength or peak absorption wavelength, is the specific wavelength at which a substance absorbs the most enenrgy. This wavelength is often used because it is the most sensitive indicator of the presence of a particular substance.

There are several reasons for using the wavelength of maximum absorbance in various applications. One reason is that it is often the most reliable and accurate way to measure the concentration of a particular substance. When a substance absorbs light, the amount of light absorbed is proportional to the concentration of that substance. By measuring the amount of light absorbed at the wavelength of maximum absorption, the concentration of the substance can be determined with high precision. Therefore, in order to better observe the efficiency of the photocatalytic process, the spectrum of the MB is measured by the spectrophotometer from the MB degradation solution series.

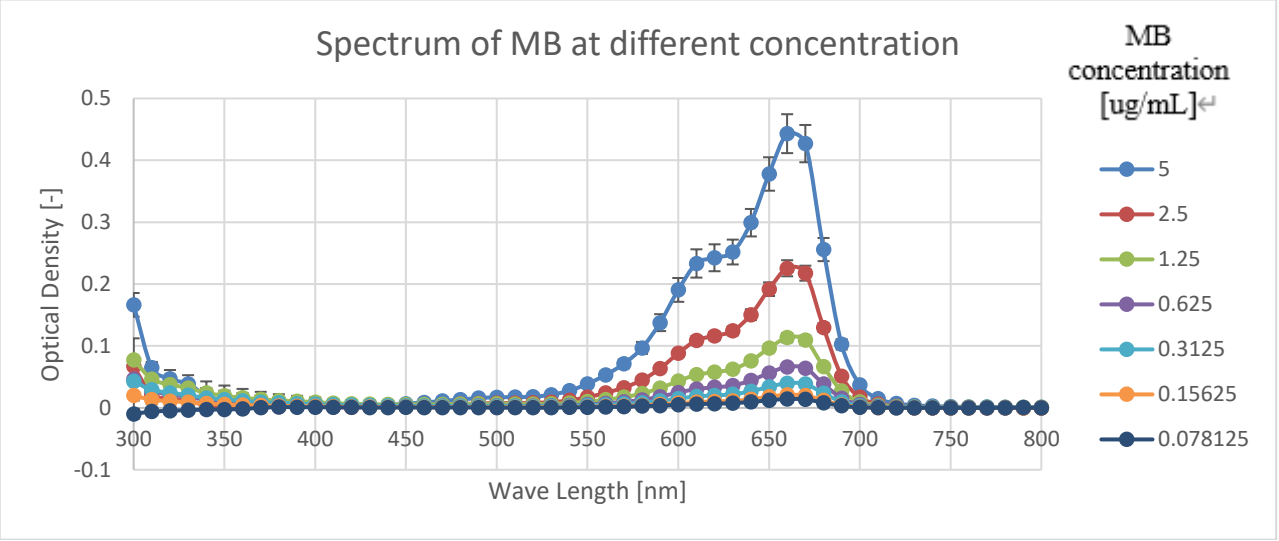


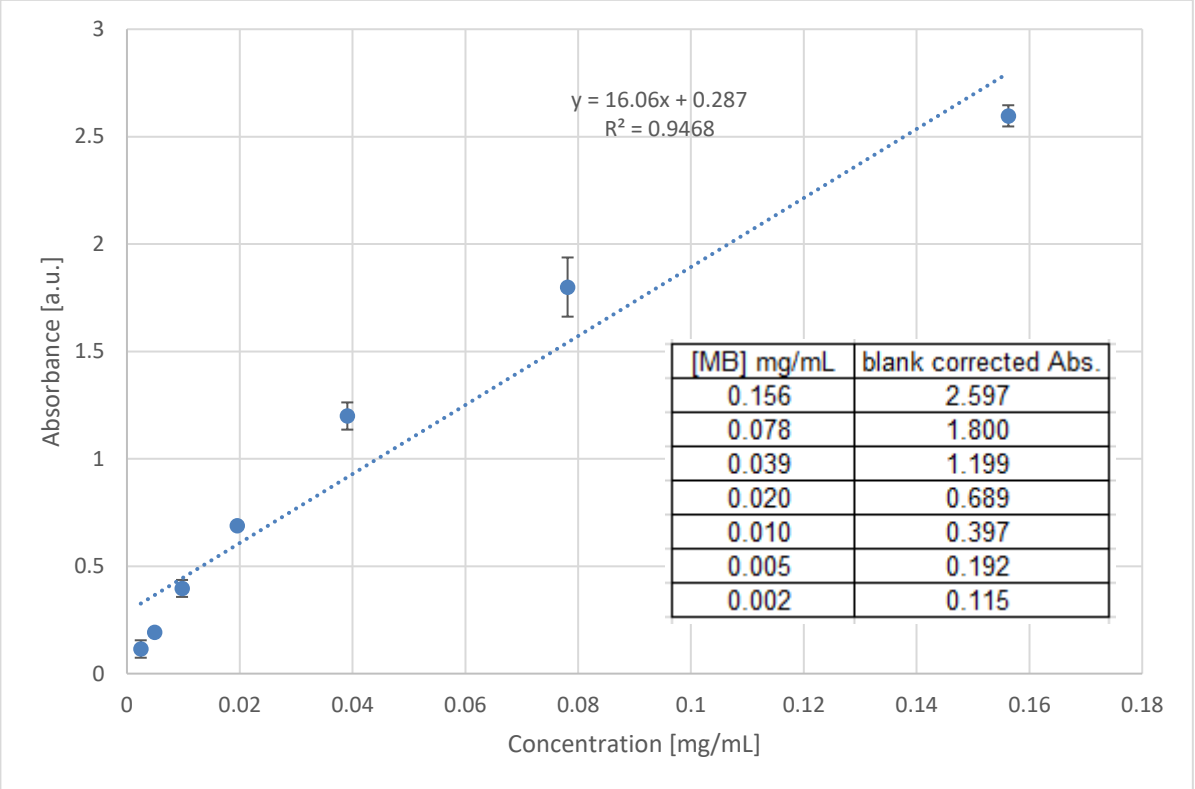
Fig. 3.1 Spectrum of MB at different concentration

In Figure 3.1, the absorbance showed a slight difference at 300 nm. The absorbance at the lowest concentration shows a negative value, and this problem may be caused by the error in the measurement itself minus the pure water control. It is clear that the MB solution achieved a maximum absorbance at 660 nm at all concentrations. Therefore, in the later experiments, we will take the concentration change of MB solution at 660 nm as the basis for judging the photocatalyst efficiency.

According to the description of Beer's law, a beam of monochromatic light irradiated on the surface of an absorbing medium, after passing through a certain thickness of the medium, as the medium absorbs a portion of the light energy, the intensity of transmitted light should be weakened. The greater the concentration of the absorbing medium, the greater the thickness of the medium, the more significant the weakening of light intensity, the expression is

$$A = K \cdot l \cdot c$$

A is the absorbance, l is the thickness of the absorbing medium, and c is the concentration of the absorbing substance. The volume of solution in each well of the well plate is 200uL, that is, the thickness of the medium is all the same.



[MB] mg/mL	blank corrected Abs.
0.156	2.597
0.078	1.800
0.039	1.199
0.020	0.689
0.010	0.397
0.005	0.192
0.002	0.115

Fig. 3.2 Dependence of absorbance of MB solution on high concentration

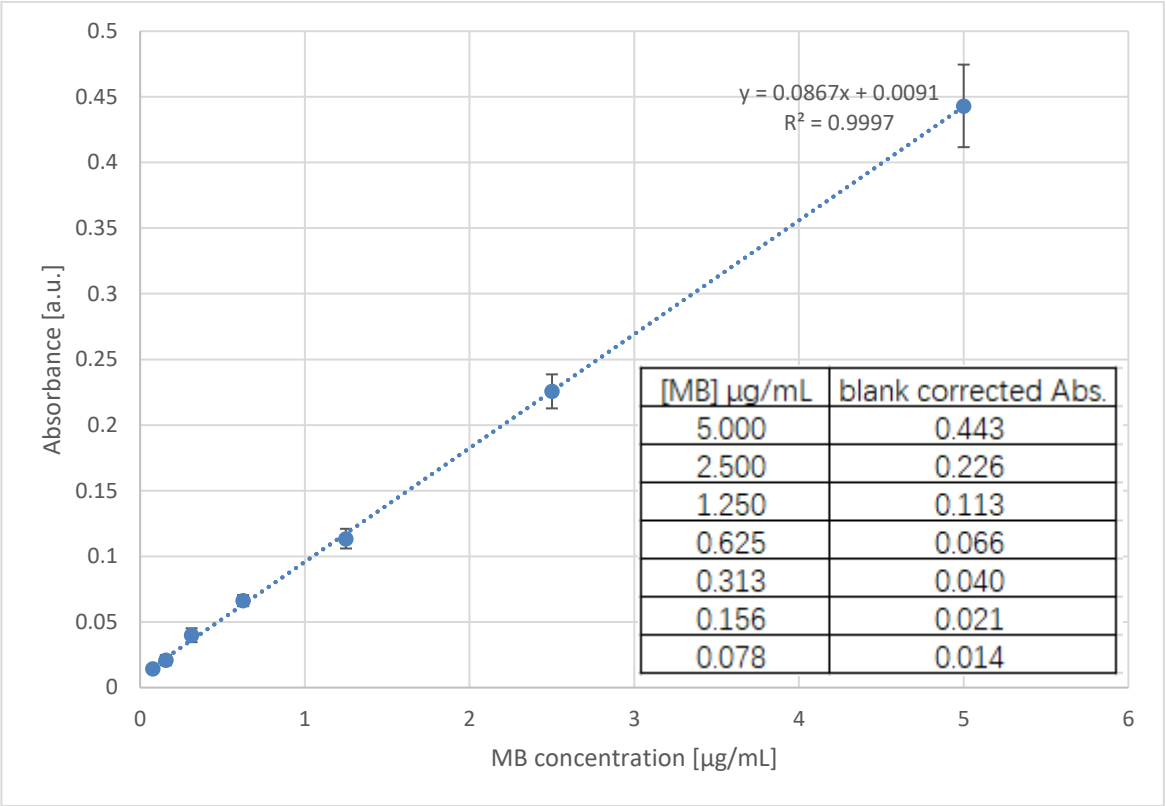


Fig. 3.3 Dependence of absorbance of MB solution on low concentration

Figure 3.2 and Figure 3.3 show the absorbance trend lines at 660 nm for different concentrations of MB solutions, respectively. The relationship between concentration and absorbance at high concentration tends to be more exponential or logarithmic function. And at low concentrations, the relationship between concentration and absorbance is more linear, which is consistent with Beer's law.

3.2 Bioreactor optimization

In order to obtain the most accurate experimental results possible, there are many factors that need to be taken into account to ensure that ZnO is sufficiently excited by photons in MB solution for photocatalysis to occur. A test based on the effect of bioreactor speed on the results is shown in Fig.3.4. The commercial ZnO for the preliminary test but GZO for the main experiments because of the low quantity of synthesized material available.

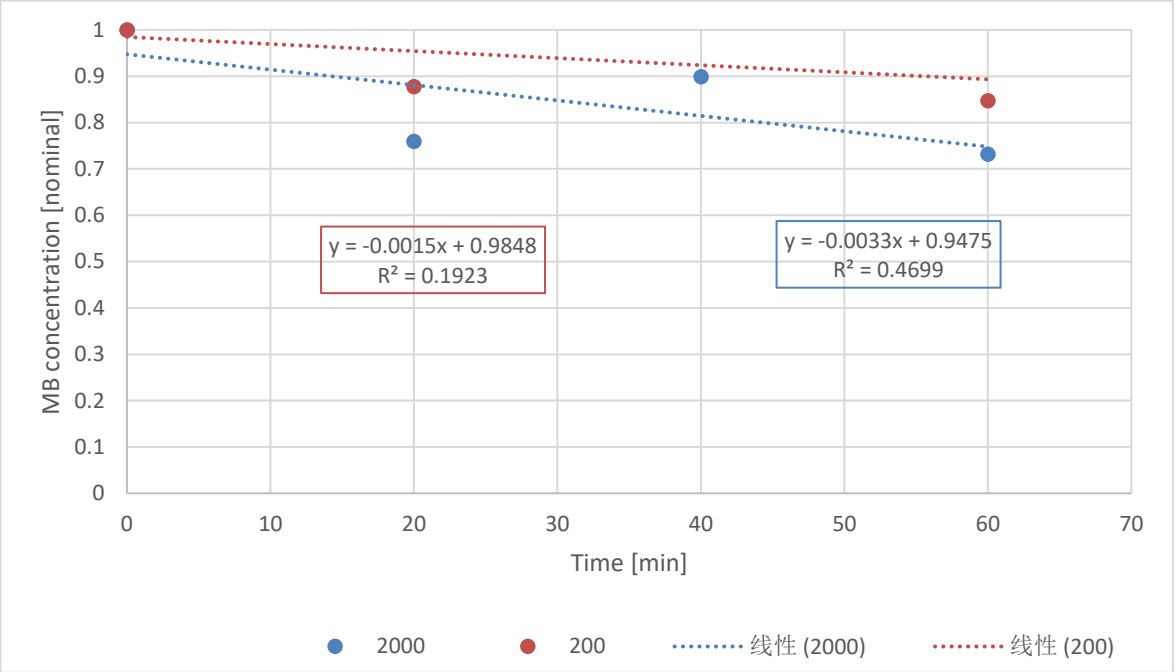


Fig.3.4 Photocatalytic degradation efficiency tested in bioreactors at different speeds

After one hour of testing, the MB concentration in the solution at 2000 rpm was approximately 10% lower than at 200 rpm. Therefore, in the later experiments, bioreactor used 2000 rpm as the test standard.

Speculation of experimental results:

The author hypothesized that it is more difficult for the GZO nanoparticles in solution to aggregate together at higher rpm. When the nanoparticles are exposed to the solution alone, the contact surface area of the particles with the reactant solution reaches a maximum. In addition, when the rate of the catalytic reaction is fast enough, the higher rotational speed results in a higher flow rate of the solution in the tube to facilitate the adsorption of GZO nanoparticles to more MB molecules.

3.3 Degradation

Figure 3.5 shows the graphs of time variation of absorbance and concentration of MB solution under four different conditions. Figure 3.6 shows more visually the variation of MB concentration after the light source KL 2500 LED is turned on.

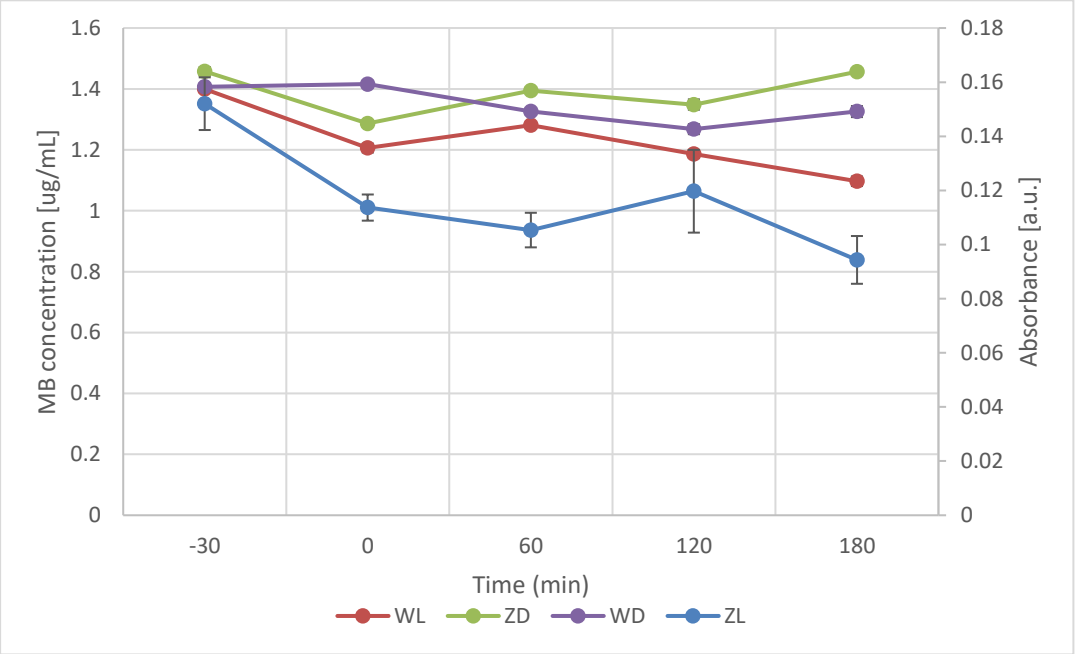


Fig.3.5 Absorbance & MB concentration versus time

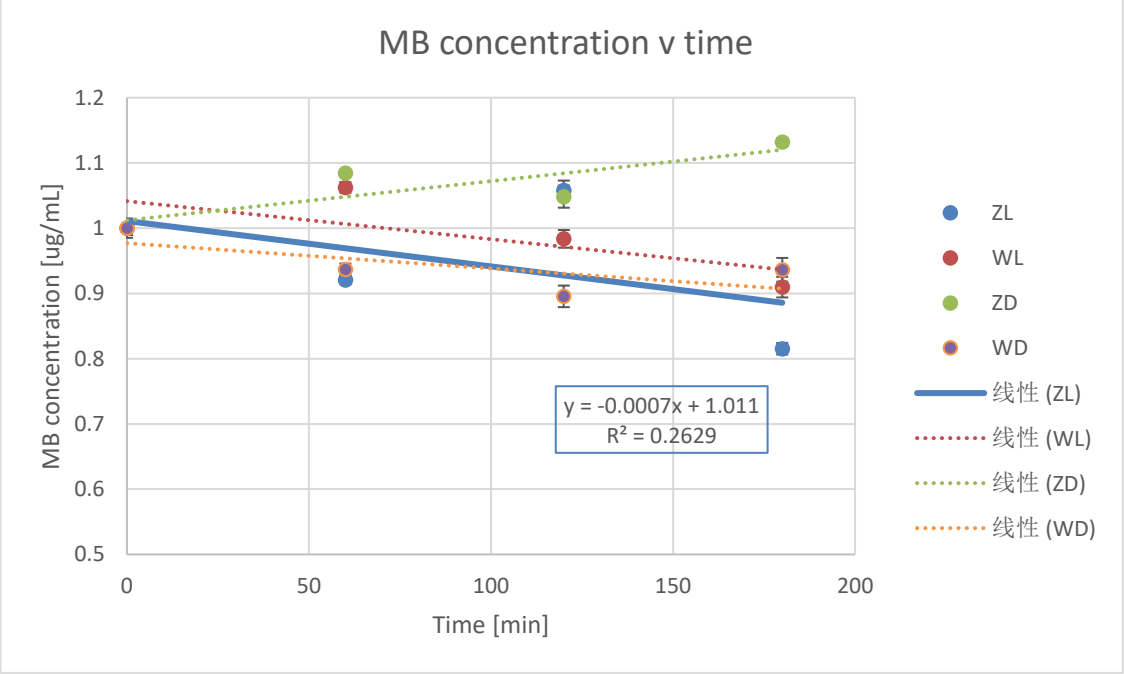


Fig.3.6 Photocatalytic degradation efficiency of GZO

First, in Figure 3.5, the start time of -30 min means that all solutions in the tubes were stirred for 30 min under the action of the bioreactor at 2000 rpm before the light source was turned on. The idea of this is to make the GZO nanoparticles in the solution uniformly distributed in the solution and for dye to absorb onto GZO's surface so that the results of the experiment can be shown faster after the light source is turned on. The reduction in MB concentration within this time could be due to dye absorption onto the nanoparticle surface. After 30 minutes of agitation, the MB solution showed different concentrations in the four groups of samples, and one of the factors causing this difference could be the normal variation with pipetting liquid.

According to the results shown in Figure 3.6, it is directly visible that the concentration of the MB solution decreases by about 20% after 180 minutes after the addition of GZO nanoparticles and visible light excitation. The overall MB concentration of the other three groups of samples fluctuates around 10%. These fluctuations can be caused by a number of factors, and may originate from the equipment itself in addition to errors caused by pipetting. The apparatus for photocatalytic experiments is customized and developed in-house, rather than an optimized device that can be purchased. Thus, the photocatalytic ability of gallium doped zinc oxide nanoparticles may have more potential than seen.

With the doping of gallium elements, the photocatalytic reaction of the catalysts can be excited by visible light. Compared to UV light, visible light has a larger wavelength

$$E = hf = \frac{hc}{\lambda}$$

According to the description in Planck's formula, the speed of light and Planck's coefficient are both constants, and the energy contained in the photon decreases with increasing wavelength. This means that the energy received by the semiconductor also decreases, while the energy required for the electron to jump from the valence band to the conduction band is presumed to decrease after gallium doping. However, this may require further experiments.

Discussion

I collected the results of other scholars' studies as a comparison after the experimental results in this paper. Figure 3.7 shows the findings of the article [35].

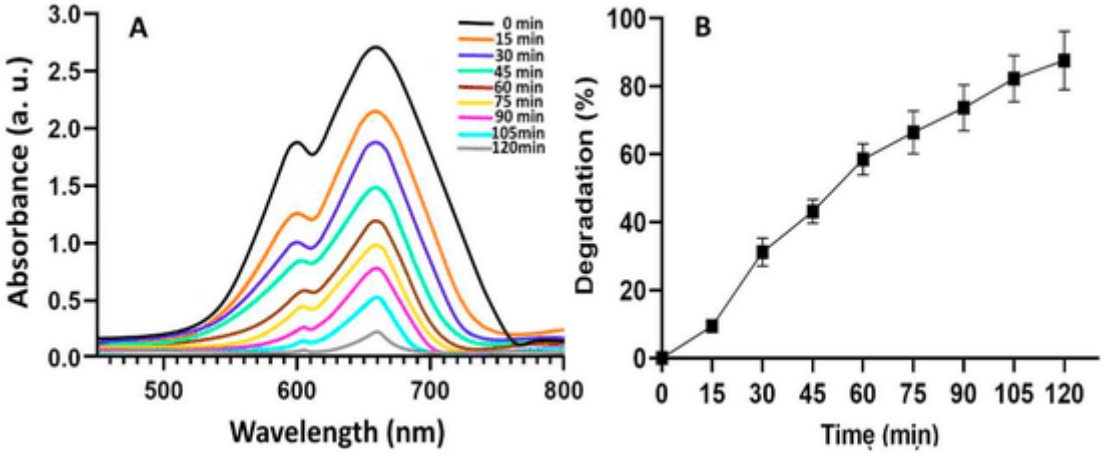


Fig.3.7 Photocatalytic activity of ZnO-NPs toward methylene blue (MB). A) Photo-assisted degradation of MB for 120 min in the presence of ZnO-NPs and B) percentage of degraded MB for 120 min. [35]

According to Figure 3.7 A, the peak absorbance of the MB solution appeared at various time points at the wavelength of 660 nm, which is consistent with the results of this paper in measuring the maximum absorbance of MB solution at different concentrations. In Figure 3.7 B, the degradation of the MB solution is about 88% complete.

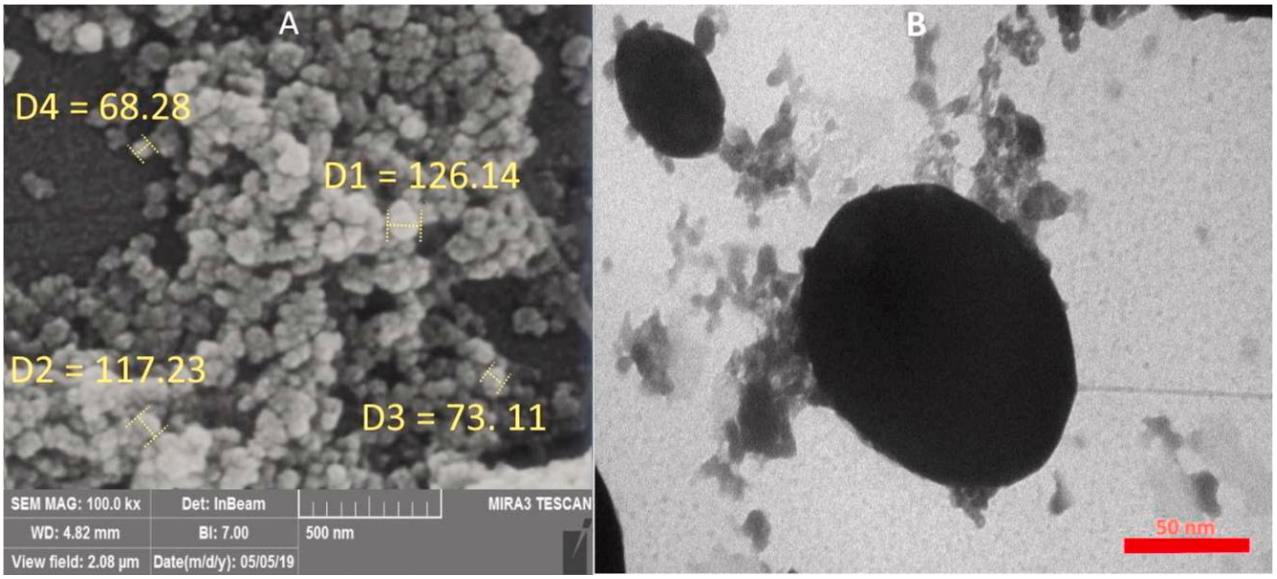


Fig. 3.8 Electron microscopy analysis of biosynthesized ZnO-NPs. A) FE-SEM micrograph, B) TEM micrograph [35]

Throughout, the degradation efficiency of GZO nanoparticles in MB solution appears to be lower in comparison with it, and the author analyzes the reasons for such differences as follows:

First, the synthesis method of nZnO nanomaterials used in the article [35] is a biological method. Figure 3.8 shows that nZnO has a spherical shape with an average size of 50-150 nm. The GZO nanomaterials used in this paper are shaped as hexagonal columns in the top view with an average length of 3-5 μm and a diameter of 1 μm (fig.2.1). According to the nano effect, the particles have a larger surface area to volume ratio at a smaller volume, which is one of the important factors affecting the photocatalytic efficiency.

At the same time, the choice of excitation light source is completely different: GZO uses visible light throughout the photocatalytic degradation process, while nZnO uses UV light with shorter wavelengths and higher energy. This is also an important research direction in this paper.

There are many other factors that affect the efficiency of photocatalysis. In terms of concentration the ratio of MB dye to GZO photocatalyst is 1:10, but the amount of nZnO solution used is not given. In addition, the influencing factors include the type of liquid, interaction kinetics, and so on, which require more experimental investigation.

The comparison here shows that although GZO can use visible light as a photocatalyst to degrade organic matter, the efficiency is still not satisfactory compared to the conventional semiconductor oxide ZnO. Therefore, the new doped photocatalyst still needs more extensive and detailed experiments to explore its potential.

Conclusion

The experimental results in this paper verify that GZO nanoparticles can undergo photocatalysis under visible light excitation, and the results are encouraging. the potential of GZO as a photocatalyst is unquestionable and ideal for optical and water treatment application.

With the increasing concern about water pollution in recent years, methods and materials for dealing with pollutants have been explored in depth. The wide distribution and easy accessibility of sunlight as an important source of renewable energy provide great potential for photocatalytic research.

Among them, the semiconductor material ZnO nano stands out as a new generation of photocatalyst material with its large surface area structure, optical and electrical properties and environmental inclusiveness. To maximize the photocatalytic efficiency of the material, a wide range of doped metals were used for research and testing. They focus on the following enhancement directions.

Increasing the surface area of nanoparticles - The number of active sites can be increased with the increase of particle surface area. Inhibition of nanoparticle aggregation is also out of this reason. The method and conditions of nanoparticle synthesis have a significant impact on the surface area and morphology. Inhibition of recombination of excited electrons and holes. Inhibits recombination of excited electrons with holes. When the electron receives the energy of the photon and is excited the electron still has a chance to recombine with the hole, while the energy is lost in the form of heat. Energy gap reduction - Increases the electrical conductivity of the material, resulting in lower energy required for electrons to be excited.

Photocatalytic processes can occur at longer wavelengths (visible light), which is the focus and expectation of this paper. Although sunlight contains some ultraviolet light, the Earth's atmosphere absorbs most of it and a much higher percentage of visible light falls to the ground. While the high-energy UV itself has a germicidal and disinfecting effect, it also has a tremendous impact on human health. Therefore, it is of great importance both for the improvement of photocatalytic efficiency and for the indoor application of photocatalysts.

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