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Study of Zinc Oxide Nanoflower for Photocatalytic Applications Prepared via Hydrothermal Method

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Abstract: Zinc Oxide (ZnO) nanoflower have been commonly studied due to its tremendous application as photocatalysts in wastewater treatment. ZnO nanoflowers contributes great properties that are low cost, high redox potential. ZnO nanoflowers were synthesized using low temperature hydrothermal method of zinc acetate dihydrate which were used as zinc oxide precursor with hexamethylenetetramine (HMTA). Different concentration of nutrient was used to perform using the hydrothermal process. To characterize the phase and crystallinity of ZnO nanoflower were studied by X-ray diffraction (XRD). These experiments implement to investigated that flower-like shape ZnO with different morphology studied by Field Emission Scanning Electron Microscopy (FESEM). The photocatalytic performance of methylene Blue (MB) for different morphology flower-like ZnO was studied.

Keywords: ZnO, Nanoflower, Hydrothermal Method, Photocatalytic

1. Introduction

The study of creativity by humans, the development of problem solutions and enhancement of industrial harvest with energy proficient and rate efficient materials have opened the paths of nanotechnology. Nanoscale playing most important role in medicine, electronic, advanced material and environmental technology.Water is the most valuable and vital resource in the world, providing for more than 75% of the land surface. The availability to nontoxic intake water is a broad need concern for endurance of human just as undomesticated life [1].

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With industrial growth, environmental pollution worsens, natural contamination intensifies and high measures of natural toxins, and this wonder is a sincere issue. Huge measures of air and land natural and poisonous toxins likewise reach waste water stream. To overcome this problem, photocatalytic with nature approachable and great competence possessions have remained use in many fields, they are ecological purification, self-cleaning material, renewable energy and etc. One of a good semiconductor photocatalyst, Zinc Oxide (ZnO) consumes be there frequently inspected because of tremendous properties that are low rate, great oxidation reduction potential, non-toxicity and environmentally friendly structures photocatalyst activity [2]. ZnO has a broad-ranging band gap (3.37 eV) and an extraordinary exaction binding energy (60 meV) it can retain a bigger part of the UV range also display a more prominent photocatalytic performance than TiO_2. ZnO have very quickens movement of electron and huge range of quantum productivity [2].

The most of photocatalytic are comprehend the connection between the structure or state of nanomaterial and their electrocatalytic properties. The application of photocatalysis take place as ZnO is irradiate by light with vitality larger than its band gap energy but inactive to fascinate visible light. ZnO have highest degradation of organic pollutants [3, 4]. The greatest technique for the grouping of various inorganic nanomaterials has accomplished being the hydrothermal process, as it helps us to deliver preferred materials under globally thoughtful conditions on the simple path.

The crystal arrangement and optical properties of ZnO nanoflowers remained characterized and the realization performance were investigated. In spite, the photocatalytic performances of ZnO nanoflowers was explored, establishing the actual photocatalytic performances aimed at the poverty of peroxides. The process of ZnO powder through hydrothermal process consumes been widely anticipated, and the ZnO powder offers abundant benefits. Hydrothermal method is a modest way to compact with set one up dimensional ZnO materials. ZnO powder is widely anticipated as an outcome of their absorbing mixture, electrical and optical properties in photocatalysis.

2. Materials and Methods

2.1 Materials

The required analytical chemicals used methylene blue (MB) dye, zinc acetate dihydrate [Zn $(CH_3COO)_2.2H_2O$], and hexamethylenetetramine (HMTA)[$C_6H_{12}N_4$]. In this experiment zinc acetate dihydrate represented as the Zinc precursor. Deionized (DI) water obtained using water purification system.

2.2 Methods

Zinc Oxide (ZnO) nutrient solution were prepared by hydrothermal method. Zinc acetate dihydrate [Zn $(CH_3COO)_2.2H_2O$] and Hexamethylenetetramine (HMTA)[$C_6H_{12}N_4$] were the two materials that used for the synthesis of ZnO nanoflower.0.22g Zinc acetate dihydrate [Zn (CH3COO)2.2H2O] were dissolved in 100ml of DI water place the stirrer inside the beaker and stirred the solution for 10minute at 300rpm.In another different beaker 0.140g HMTA[C6H12N4] were dissolved in 100ml of DI water place the stirrer inside the beaker and stirred the solution for 10minutes at 300rpm.

Then mixed the both solution and pour inside the reagent bottle. Place the reagent bottle solution inside hydrothermal oven at 90℃ constant temperature for 3hours.After 3hours take out the reagent bottle and cooled down at least 2hours at room temperature. The upper liquid was decanted off and the white slurry sample were collected by filtration method using Whatman filter paper. Finally, place the sample at furnace oven dried at 60 ℃. Repeat the procedure to prepare different concentration for 30mM ,50mM and 70mM ZnO nanoflower powder for characterization. All processes are summarized in Figure 1.

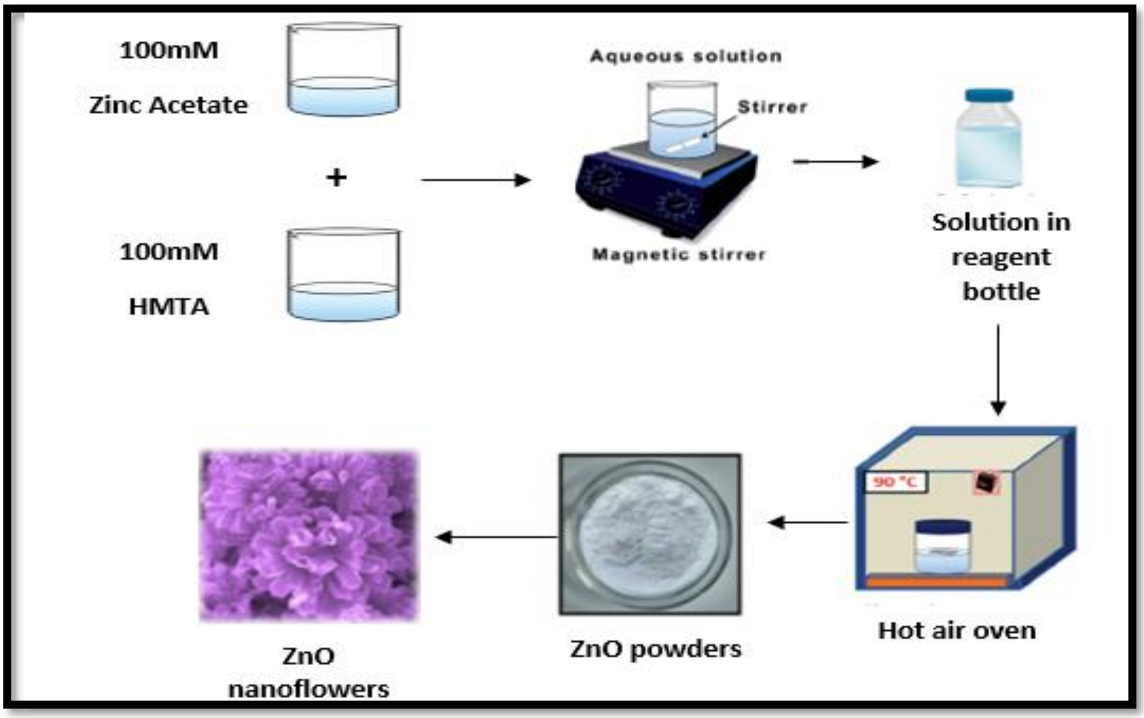

Figure 1: Modified process flow of hydrothermal method [3]

2.3 Characterization

The Zinc Oxide (ZnO) nanoflower were characterize by different techniques. The crystallinity and phase analysis were examined by X-ray diffractometer (PANalytical, Netherlands) were used to study the structural characterization. The different morphological structure of ZnO were analyzed using Field Emission Scanning Electron Microscope (JEOL-JSM 7600F). The formation on ZnO nanoflower and the concentration of Methylene Blue (MB) dye at regular intervals were studied by a UV-Vis spectrophotometer (Shimadzu UV-1800).

2.4 Photocatalytic performance of ZnO nanoflower

By photocatalytic performance of the zinc oxide (ZnO) nanoflower were deliberate by UV light enables the methylene Blue (MB) dye to degrade. The photocatalytic experiments were conducted in the entire set were kept in a box accented by black paper. The ability of the specimens to degrade and decolorize were inspected by MB dye. 1mg of MB dye stuff was completely dissolved in 100 ml DI water after 40 minutes of mixing the solution.

Add 0.10 gm of catalyst above mentioned MB solution and measure the extent of degradation, stir in the dark for absorbing and re-absorbance durability. To predict the amount of degradation, solution samples were taken at 20-minute intervals and recording the absorption intensity using UV–vis spectroscopy. There, the efficiency of catalysts can calculate using the equation 1:

$$\text{MB degradation (\%)} = \frac{C0 - Ct}{C0} \times 100 \qquad \text{Eq. 1}$$

The absorbance before and after concentration at time t is represented by C0 and Ct.The degradation efficiency of MB dye was investigated using ZnO nanoflowers were produced with varied concentration using a hydrothermal technique. Density, thickness, and defects states all have an impact on the efficiency degradation rate.

3. Results and Discussion

3.1 Structural analysis

Figure 2 below represented the XRD patterns of ZnO nanoflowers.Only a large peak between 31.7 ° and 36.1 ° was found in Figure2 for the ZnO nanoflower developed at 90 °C , showing that the ZnO nanoflowers generated at this temperature have a high crystallinity..The XRD patterns of crystalline ZnO structure show peaks at 31.7°, 34.5° and 36.1° which relates to the lattice plane (010), (002) and (010). This pattern is well matched with Joint Committee on Powder Diffraction Standard, (JCPDS) data and this ZnO were consists of nanoflowers arrays that contain wurtzite structure phase of ZnO. Besides that, the peak at 31.7° with orientation plane (010) showed the highest intensity for wurtzite ZnO nanoflower arrays compared to the other peaks.

The wurtzite (010) crystal structure is allocated as the special development for the hexagonal wurtzite planes of Zinc Oxide due to the direction with great crystallinity [5]. The crystallinity of the ZnO nanoflowers improved in accordance with increase in peak intensity.Table 1 show the presence of numerous point defects and threading dislocations is most likely due to the experimental lattice parameter deviating from the wurtzite crystal.

The crystallisation of the ZnO nanoflowers increased in accordance with the increase in peak position. In spite of, the sample obtained from this study show that 50mM concentration as it gives the highest crystallinity and it was the lowest value of FWHM in Table 1. Furthermore, as the concentration increased, the intensity of the significant diffraction peaks decreased, and the peaks shifted to a lower angle.These findings suggest that the lattice parameter value of ZnO was altered as a result of changes in crystalline quality and crystalline size.

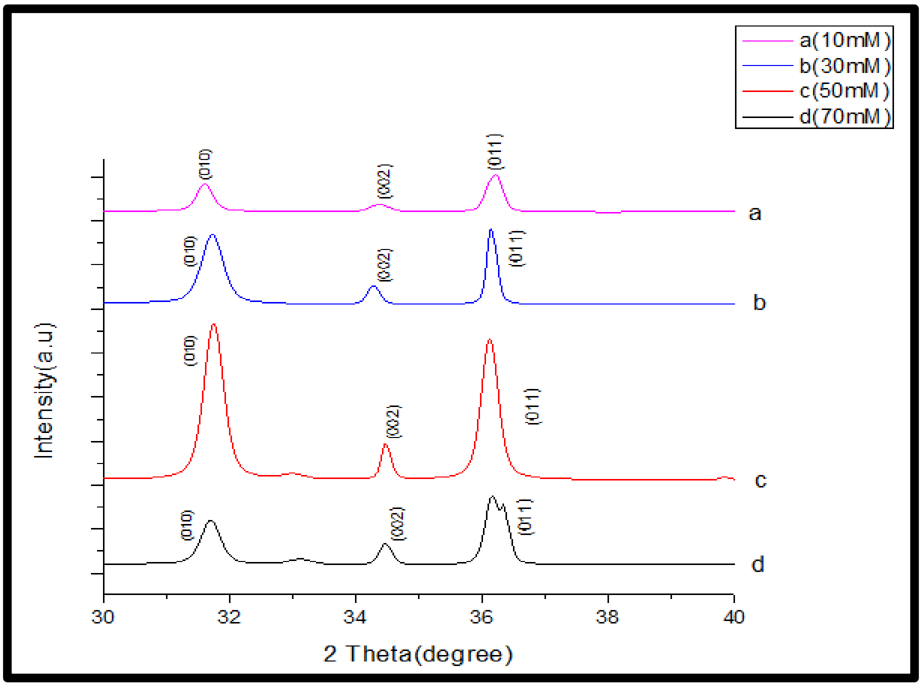

Figure 2: XRD profiles of the various concentration of ZnO solution. (a)10mM, (b)30mM, (c)50mM and(d)70mM at 90℃

Besides, the Equation 2 show that Scherrer formula is used to calculate the average crystalline size(D) [6].Where is the θ is the Bragg's angle in degrees, K is the configuration of factor (0.9),β is the FWHM in radians , and λ is the wavelength of X-ray radiation (= 1.5416A). Furthermore, the FWHM of the (011) plane was included in the above computation because it has a high intensity and shows a substantial change as the concentration value is increased using the hydrothermal method.

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad \text{Eq. 2}$$

Table 1: Value of FWHM for ZnO nanoflower arrays from XRD analysis

2θ(degree)	**FWHM (°)**	**Size(nm)**
31.7000	0.3936	22
34.2548	0.1968	43
36.1217	0.1378	62

3.2 Morphological analysis

Figure 3, 4 and 5 shows the FESEM images of hydrothermally grown ZnO nanoflowers. The Field Emission Scanning Electron Microscopy (FESEM) is used to identify the surface morphology of the prepared wurtzite structure Zinc Oxide (ZnO) powder. Figure 3, 4 and 5 represent the images for FESEM of top view at x100000, x25000, and x50000 magnifications of various ZnO powder concentration solution. The observation from figure 3.0, 3.1 and 3.2 that the sample with 50mM concentration of ZnO solution.

The wurtzite phase ZnO nanoflowers powder is the first material with high surface area. Foremost, huge quantity of ZnO nanoflower will contribute better surface area. The shape of the nanoflower developed extra clear and high-pitched at the circumference of atoms to rise the competence with rise in different concentration amount of ZnO solution. The concentration of Zn^{2+} and OH^{-} as well as the hydrothermal temperature, play a vital role in the creation of the flower-shaped nanostructure of ZnO. The growing mechanism of ZnO nanoflowers was also documented by Pan et al.[7].

From the figure below analysis in the different thickness of ZnO surface morphology is the maximum width of the thickness of ZnO nanostructured is achieved at 181nm which can proved that from the Figure 3 shows the sample with 50mM ZnO solution. The experimental study revealed that when the diameter of ZnO nanoflowers increases somewhat while the concentration of ZnO solution increases, as stated by the top end of ZnO nanostructured in the FESEM image. We can see that when the concentration of ZnO solution increases, the size and structure of ZnO nanoflowers grows. We can observed that, slight changes in size and structure for the 10mM,30mM and 70mM.

3.3 Photocatalytic activity

Figure 6 shows the UV-Vis spectra of all samples. According to photocatalysts analysis the degradation rate of MB is plotted against time to notice the photocatalytic effectiveness of the ZnO, in the existence of UV light irradiation and in placed in dark surroundings. Beside that, when exposed to UV light, the MB dyestuff at 665nm was measured to indicate material degradation rate. The absorbance spectra of MB solution were varied under UV light irradiation with various ZnO nanostructures in the wavelength range 500nm to 700nm. As previously stated, the absorption peak intensity is used to identify dye degradation.

This proved that ZnO have a prospective application of ZnO nanoflower in the wastewater treatment. From this we can observed, that ZnO is a good photocatalyst. The rate of recombination of the charged carriers determines how quickly the organic dye degrades. The photocatalytic oxidation process occurs when light with an energy greater than or equal to the semiconductor band gap stimulates the separation of electrons from the valence band (VB) to the conduction band (CB) following an equal number of holes in the valence band.

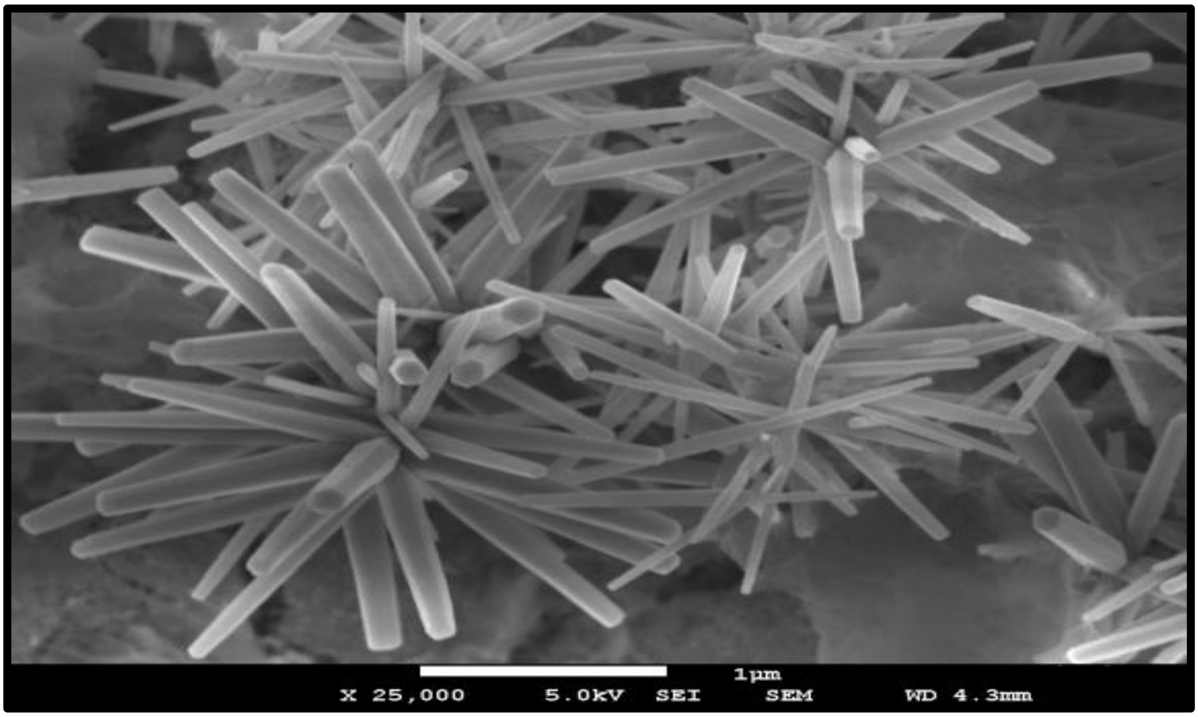

Figure 3: FE-SEM images of ZnO nanoflower grown for 50mM concentration upper vision at x25000 magnification

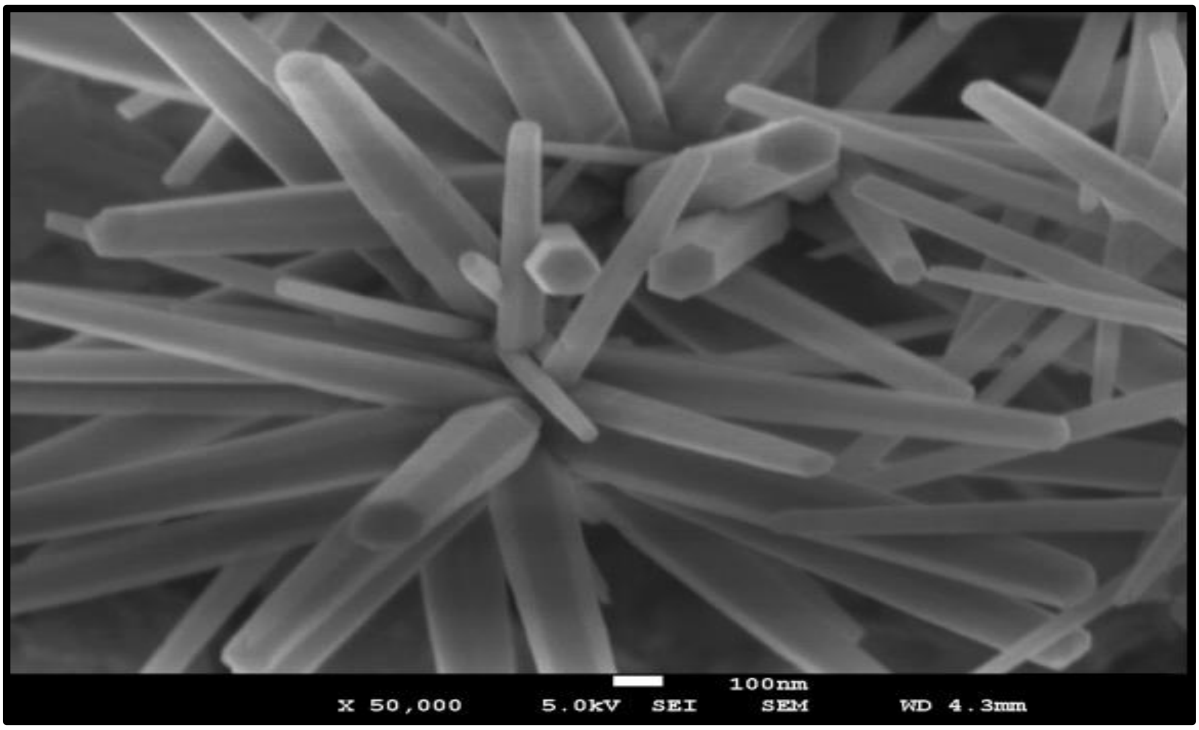

Figure 4: FE-SEM images of ZnO nanoflower grown for 50mM concentration upper vision at x50000 magnification

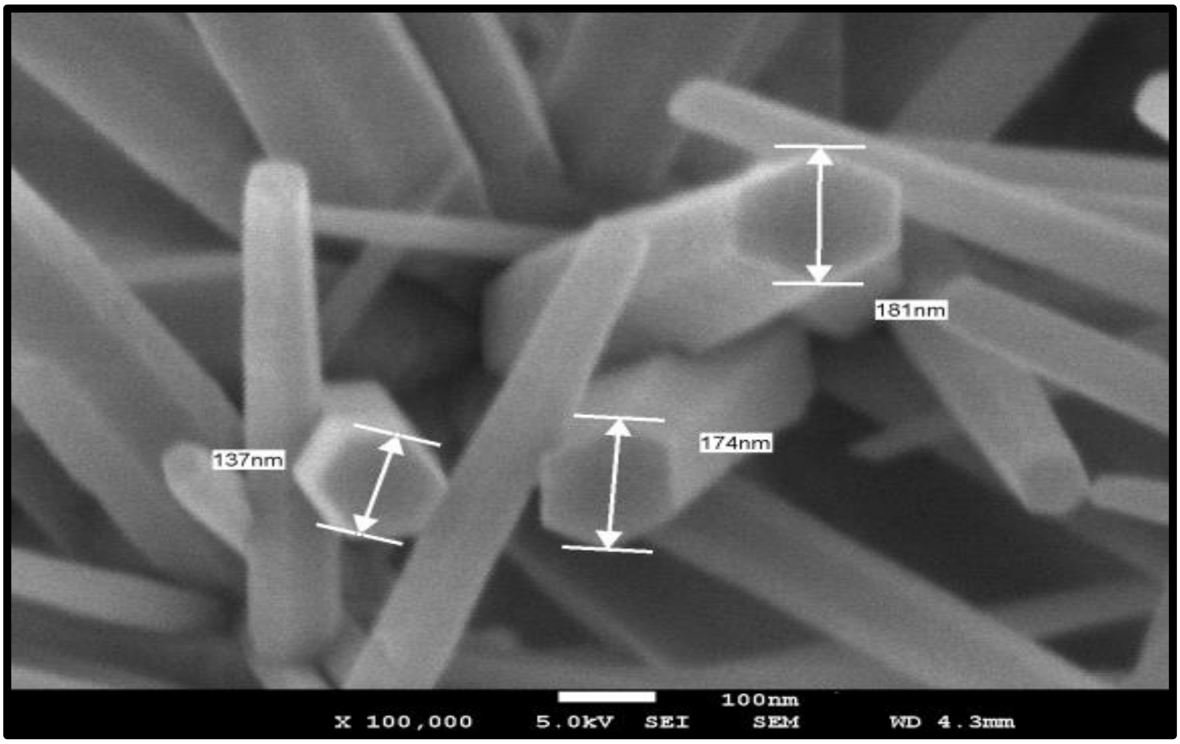

Figure 5: FE-SEM images of ZnO nanoflower grown for 50mM concentration upper vision at x100000 magnification

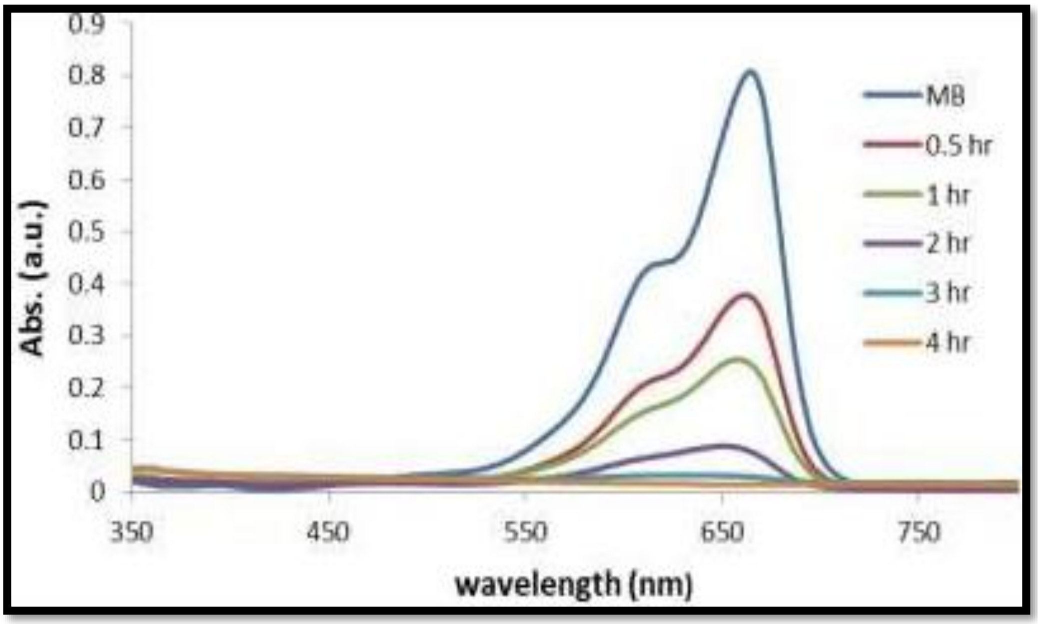

Figure 6: The UV-Vis spectroscopy of photocatalysts [20]

4. Conclusion

In conclusion, ZnO nanoflowers were fabricated using a low-cost hydrothermal approach. The XRD pattern shows that nanoflowers produced at 90℃ were pure wurtzite with good crystallinity. Aside from that, differing concentrations play an important role in the development of distinct nanoflower patterns. Crystallinity of the flowers improves with increase of concentration value. FESEM images indicate that when the concentration rises, the flower's morphology grows along with it. Furthermore, ZnO nanoflowers displayed significant photocatalytic activities in these studies, with ZnO nanoflowers grown at 90℃ demonstrating greater degradation efficiency. Oxygen vacancies and oxygen interstitials were assumed to be the active sites of the ZnO photocatalyst. The capacity to degrade MB is dependent on UV illumination period, ZnO nanoflower size, and shape. The ZnO has a broad application in waste.

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