Journal Homepage: - www.journalijar.com
INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)
Article DOI: 10.21474/IJAR01/3990
DOI URL: http://dx.doi.org/10.21474/IJAR01/3990
ISSN NO. 2320-5407

RESEARCH ARTICLE

PHOTOCATYLITIC DEGRADATION OF METHELENE BLUE DYE USING ZnO NANORODS AND SUN LIGHT.

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Manuscript Info

Manuscript History

Received: 08 February 2017
Final Accepted: 16 March 2017
Published: April 2017

Abstract

The ZnO nanorods have been successfully synthesized by seed layer preparation using dip coating method and by growth layer preparation using hydrothermal method. The prepared ZnO nanorods were characterized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and UV-Visible spectrophotometer (UV-Abs).. These ZnO nanostructures were explored as catalyst for solar-light induced photo catalytic degradation of methylene blue dye in an aqueous solution. The degradation rates depend on the dye structure, concentration, solvent-dependent ZnO film morphologies, pH of the medium and excitation light source. The photocatalytic performances of the obtained ZnO nanorods were deeply investigated for possible application of textile/water treatment.

Introduction:-

The ZnO have been widely used metal oxide semiconductor material for photo catalysts processes. The ZnO have a band gap of about 3.38 eV and high exciton binding energy of 60 meV.[1] The synthesis of ZnO nano particles with different morphologies and sizes were made by researches. One-dimensional nanostructures (e.g., nano wires, nanorods, nano needles, nano tubes, columns and helices) play an important role in many applications because they possess high surface to volume ratio with short diffusion length area.[2-5].The one-dimensional nanostructures have large junction area which imparts low reflectance provide a direct pathway for charge transport [6].Also, these materials reduce the recombination of excitons and thus show high energy conversion efficiency and since ZnO has a wide band gap, its use is restricted to the visible region.

The photo catalytic activity of the investigated materials was tested by the degradation experiments, the samples were irradiated by solar light for 120 minutes in order to remove the hydrocarbons from the sample surface.. The glass substrates were dipped in methelene blue aqueous solutions where samples are immersed was irradiated by a solar light. The irradiated solution was measured at regular time intervals with an UV Vis spectrophotometer JASCO-570 UV-Vis spectrophotometer. Degradation of methelene blue was evaluated by the absorption peak at 655nm. The photo degradation reaction was calculated from the linear plot of ln [Co/C] versus from the irradiation time. The decomposition of the methelene blue in the absence of any photo catalyst materials was checked as a reference. [7-8]

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Experimental Technique: Seed Layer preparation:-

The ZnO nano rods were deposited by dip coating process / hydro thermal technique. Initially the seed layer solution was prepared for 0.1 mol concentration by mixing Zinc acetate (0.2 gms) and Ethanol (10 ml). The initial pH of solution is 7.5. The solution was mixed in a magnetic stirrer for 2 hours. The 0.25 ml of de-ionized water added to the prepared solution drop by drop in the mixer. The prepared seed layer solution was used for producing ZnO seed coated thin films using automatic dip coating machine. The dipping time and retrieval time was set to 1 min and 15 minutes set to 70 °C for drying. The same process was repeated for 5 times to get desired thickness. After that the seed coated glass substrates were kept in muffle furnace at 200°C for 1 hour annealing and left it for auto cooling until it reaches room temperature. The same seed coating process was repeated for different values pH 8.5, 9.5 and 10.5.

Growth Layer Preparation:-

In this process, The ZnO nano rods were over the seed layered ZnO by using the materials zinc nitrate, hexamethylenetetramine and deionized water. All these materials were put it into the beaker and mixed in magnetic stirrer for 2 hours at room temperature. After preparation of growth layer solution it was taken in a beaker and the seed coated substrates are dipped inside the growth solution and kept in oven at 90°C for 4 hours. After that the slides were taken out from the beaker and rinsed in water for separation of residuals. These substrates are kept in 500°C annealing process for 1 hour. The ZnO nanorods were prepared for four different pH values of 7.5, 8.5, 9.5 and 10.5.

Before involving seed layer preparation, the substrate cleaning plays a vital role in the deposition of thin films. First, commercial microscopic glass slides were boiled in chromic acid for 2 hours, washed with detergent, rinsed three times in acetone and finally ultrasonically cleaned with distilled water before deposition.

Results and Discussion:-

X-ray Diffraction (XRD):-

The XRD patterns of pH 7.5,8.5,9.5 and 10.5 termed as A1, A2,A3 and A4 is as shown in figure 1.At pH 7.5, the patterns of the ZnO nanorod array films deposited on glass revealed three dominant peaks at 2θ values of 31.61°, 34.29° and 36.11° corresponding to (100), (002) and (101) planes respectively. The (h k l) peaks are in good agreement with the standard JCPDS 036-1451 card for hexagonal wurtzite ZnO. The XRD pattern of pH 7.5 shows that, it has a strong (002) peak and weak (100) and (101) peaks. The strongest reflection observed along the (002) plane for pH 7.5 sample indicates that the ZnO nanorods arrays are preferentially well-oriented in the direction of the c-axis. The presence of broad peaks in the pH 7.5 samples shows that the grains have started to grow on pH and the films are of nano crystalline nature.

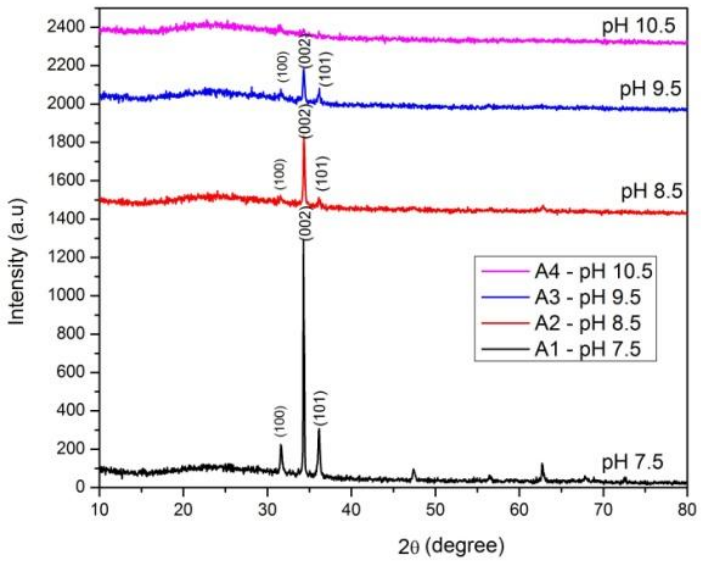

Fig.1:- XRD patterns of ZnO nanorods at different pH values.

The strong and narrow diffraction peaks indicate that the material has a good crystalline and size [9-11]. The full width at half maximum (FWHM) and grain size of crystallites was calculated using Debye Scherer's formula for (002) plane was given in Table 1. FWHM of ZnO thin films show changes with changing pH values. From fig.1 the intensities of the reflection peaks changes as the pH increases from 7.5 to 8.5, the intensity of the (100), (002) and (101) peaks has been decreased. When the pH value increased from 8.5 to 9.5, the intensity of the (100), (002)and (101) peaks has been decreased and detected at 2θ values of 31.58°, 34.33°, 36.12°.

Table 1:- The structural parameters of ZnO thin films.

Sample	FWHM	2θ (angle)	Grain size d (nm)
pH 7.5	0.08	34.29	94
pH 8.5	0.15	34.33	50
pH 9.5	0.23	34.30	33
pH10.5	0.3	36.12	25

From the table 1 it is clearly shown that as pH value increases from 7.5 to 9.5 the grain size decreased from 94 to 25. At pH 10.5 the crystal size is decreased to 25, because the c-axis orientation is decreased.

Scanning Electron Microscopy (SEM):-

Surface morphology was examined by a (JEOL JSM 5610) scanning electron microscope. The figure 2 (a-d) shows the SEM images of ZnO nanorods prepared at pH values of 7.5, 8.5, 9.5 and 10.5. They show the dense arrays of hexagonal ZnO nanorods having different diameters that are formed under different pH. The pH of the precursor solution was found to play a major role in the deposition of ZnO nanorod arrays. As can be seen from SEM images, the orientation of the obtained ZnO rod arrays strongly depends on the pH of the starting solution.

From SEM picture (Fig 2a), it can be seen clearly that the samples produced from solution with pH 7.5 well aligned nanorods were grown and they were oriented towards the vertical direction (C-axis). The density of the rods grown is decreased and diameter of rod size is decreases as the pH increases. From fig.2b to 2c it is clearly seen that as the pH increased from 7.5 to 8.5 and 8.5 to 9.5 we observe that it consist of well aligned nano granules. As pH increased from 9.5 to 10.5 in fig 2d, the rod formation has been collapsed. The reason for this should be higher reaction rate, when precipitates start to dissolve. The SEM results are in accordance with the XRD.

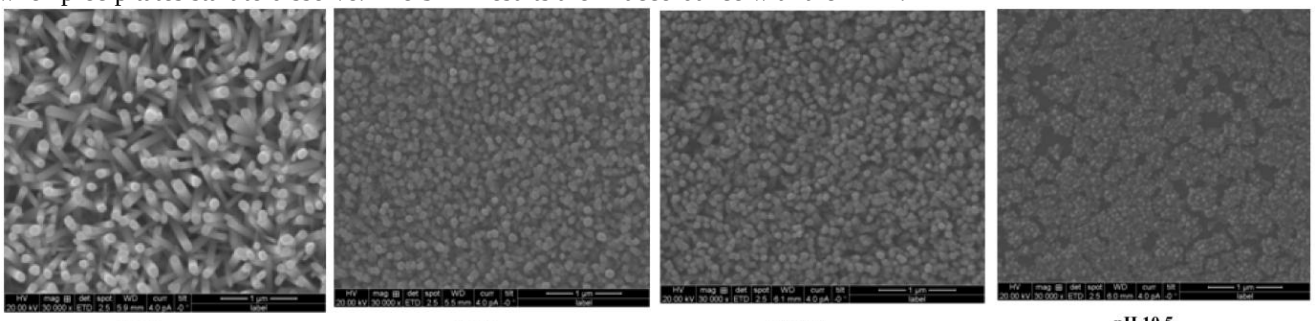

Fig.2:- SEM images of ZnO nanorods at different pH values.

From SEM observations, it is clear that the morphological characteristics of ZnO can be controlled by the pH value of starting solution. In addition, as clearly seen from SEM images, although the shape of the structures remains the same their overall dimensions change with increasing pH. In other words, one can tune-up the size of the ZnO structures from macro to nanorods by adjusting the pH of the solution [12-14].

UV-Visible Spectroscopy: Absorption:-

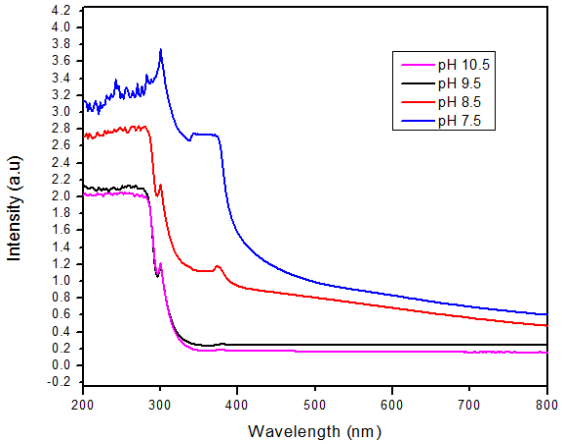

Fig. 3:- Absorption spectra of ZnO nanorods at different pH values

Absorption studies of the ZnO nanorods are further checked by optical properties. The optical absorption spectrum is as shown in the figure 3. The studies were performed in the wavelength range of 200 to 800 nm. From the result it is observed that at pH 7.5 the intensity is high. As the pH value increased from to 8.5 and to 9.5 the absorption intensity is decreased. At pH 10.5 the intensity is further decreased.

UV-Visible Spectroscopy: Transmittance:-

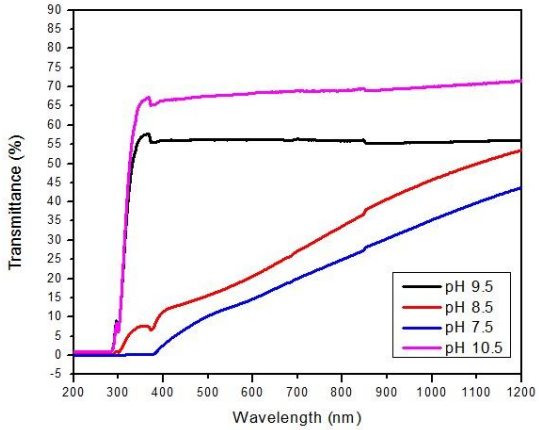

Fig 4:- Transmittance spectra of ZnO nanorods at different pH values.

Transmittance studies of the ZnO nanorods were shown in the figure 4. The percentage of transmittance is very low for 7.5 pH. The lower absorption and higher transmittance in the visible region observed in the pH range 7.5, illustrates the good optical quality of the crystals with low scattering and absorption losses which leads to industrial application especially as a transparent electrode. As the pH increases from 7.5 to 10.5, through 8.5 and 9.5 the value transmittance percentage increases.[15-18]

Photo Degradation of Methelene Blue

The Photo degradation of methylene blue under sunlight of ZnO nanostructures was investigated through photo catalytic activity. All the photo catalytic reactions in the present study were carried out under direct sunlight between 11:00 a.m and 1:00 pm. In a typical experiment, ZnO coated glass substrates were dispersed in 40 mL methylene blue aqueous solution and stirred in dark for about 15 min to allow adsorption equilibrium between the dye and the catalyst. The beaker was kept under sunlight for irradiation and withdrawn at periodic time intervals, centrifuged and the supernatant solutions were analyzed using a UV–Vis spectrophotometer. The catalytic experiments were carried out under similar conditions using pure ZnO nanorods. A blank reaction was also

performed without using any catalyst. The degradation efficiency of methylene blue was calculated using the formula given below.

% Degradation C=Co-C/Co*100

where Co = is the concentration of methylene blue at its adsorption equilibrium
C = is the concentration of methylene blue at different illumination times.

The methelene blue dye was prepared in three different molar concentrations of 4PPM, 6PPM and 8 PPM. The photo catalytic activity towards the degradation of methelene blue of ZnO samples depend upon varying the irradiation time. The first test was performed when a significant decrease in the methelene blue concentration is clearly observed when sun light between 11 a.m to 11.15 a.m. It confirmed that photocatalytic activity increases with the irradiation time. In particular after 1 hour to 1.30 hours of the solar irradiation the methelene blue dye was degraded with 95% efficiency.

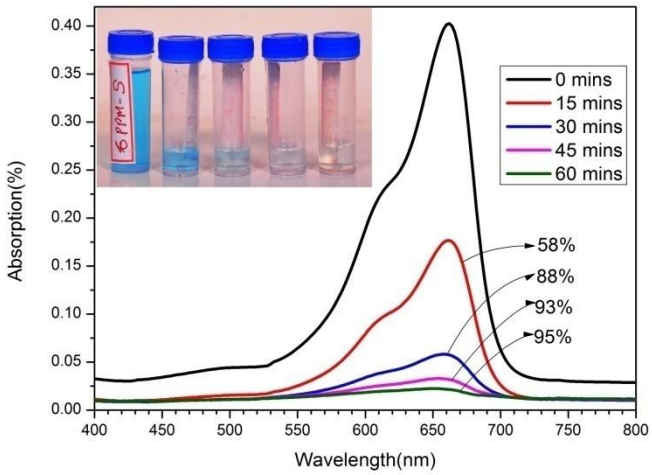

Fig. 5:- Time-dependent UV–Vis absorption spectra for decolorization of methylene blue (6PPM) using ZnO nanorods and solar light.

Fig. 5 shows the time dependent UV–Vis spectra of methylene blue dye during photo irradiation with ZnO nanorods. The molar concentration of the methelene blue dye was 6PPM and the solar light was used. The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak was observed at λ_{max} i.e., 665 nm which decreased gradually with increase in irradiation time from 0 to 60 minutes with regular intervals of 15 minutes, indicating that the dye had been degraded. The decolorization of dye was achieved as 58%, 88%, 93% and 95% for the irradiation time of 15min, 30min, 45 min and 60 min respectively.

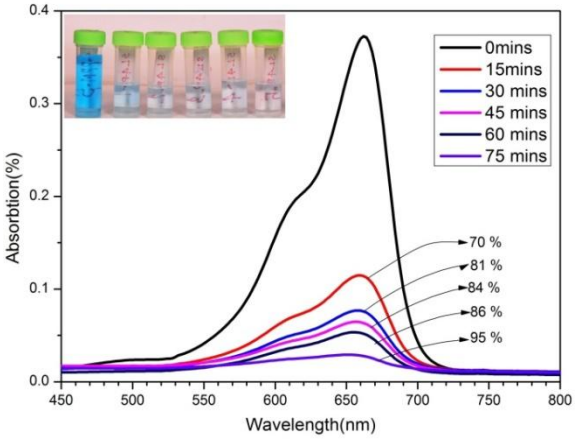

Fig. 6:- Time-dependent UV–Vis absorption spectra for decolorization of methylene blue (4PPM) using ZnO nanorods and solar light.

Fig. 6 shows the time dependent UV–Vis spectra of methylene blue dye during photo irradiation with ZnO nanorods. The molar concentration of the methelene blue dye was 4PPM and the solar light was used. The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak was observed at λ_{max} i.e., 665 nm which decreased gradually with increase in irradiation time from 0 to 75 minutes with regular intervals of 15 minutes, indicating that the dye had been degraded. The decolorization of dye was achieved as 70%, 81%, 84%, 86% and 95% for the irradiation time of 15min, 30min, 45 min, 60 min and 75 min respectively.

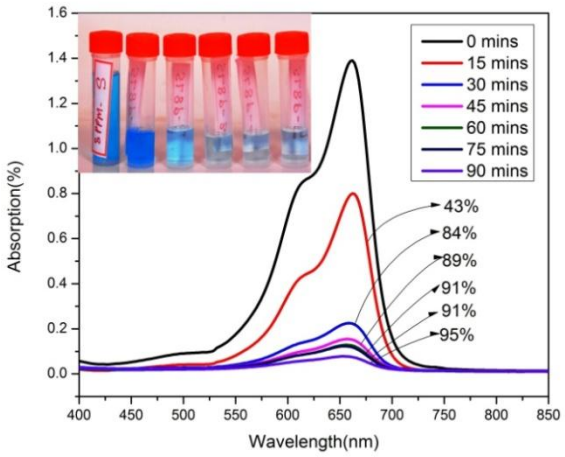

Fig. 7:- Time-dependent UV–Vis absorption spectra for decolorization of methylene blue (8PPM) using ZnO nanorods and solar light

Fig. 7 shows the time dependent UV–Vis spectra of methylene blue dye during photo irradiation with ZnO nanorods. The molar concentration of the methelene blue dye was 8PPM and the solar light was used. The rate of decolorization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak was observed at λ_{max} i.e., 665 nm which decreased gradually with increase in irradiation time from 0 to 90 minutes with regular intervals of 15 minutes, indicating that the dye had been degraded. The decolorization of dye was achieved as 43%, 84%,89%, 91% ,91%, and 95% for the irradiation time of 15min, 30min, 45 min, 60 min, 75 min and 90 mins respectively.[19-20]

Conclusion:-

ZnO nanorods grown by chemical bath deposition had shown excellent photo degrading properties towards methylene blue dye. Methelene blue dye was taken in three molar concentrations of 4PPM, 6PPM and 8PPM. Sun light was taken as light for degradation. The efficiency of the methelene blue dye degradation was 100% for all the molar concentrations, but the irradiation time was the only difference. 4PPM dye was degraded in 60 minutes, 6PPM dye was degraded in 75 minutes and 8PPM dye was degraded in 90 minutes. Finally 95% photocatalytic efficiency was got in all the three concentrations and molar concentration influence the degradation of methelene blue with irradiation time.

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