PREFACE

Semiconductor materials are always a research focus in material science due to their unique electronic, optical properties and extensive applications. In these materials, wide and direct band gap semiconductors are of great interest in photo catalysis with Zinc oxide (ZnO) representing a perspective field. ZnO, a wide and direct band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV) [1] has already been widely used in piezoelectric transducers, gas sensors, optical waveguides, transparent conductive films, varistors, solar cell windows, bulk acoustic wave devices and photo catalytic activities [2–7]. ZnO can be more efficient in the photo catalytic degradation of some dyes in aqueous solution [8]. One dimensional nano structures, such as nanowires and nanorods offer higher surface to volume ratio compared to nano particle coatings on a flat surface [9]. Over the past decades, ZnO crystallites had been obtained by several preparation approaches including sol–gel method [10], evaporative decomposition of solution [11], wet chemical synthesis [12], gas-phase reaction [13] and hydrothermal synthesis [14] etc. A variety of morphologies including nano rods [15] and nano wires [16] were synthesized.

Among the above methods, hydrothermal synthesis route is an important and low cost method for preparing ZnO nanorods and has been attracting material chemists’ attention. Many attempts have been made to study and compare the photo catalytic activity of different semiconductors and found ZnO to be one of the most effective catalysts [17]. ZnO nanorod arrays could potentially be a very good class of catalysis support structures, because of the ultra-high surface area [18]. In the present work, ZnO seed layers were prepared employing zinc acetate and ethanol as the reactants. ZnO nanorods were grown by a simple hydrothermal method employing zinc nitrate and hexamethylenetetramine as the reactants, for different growth concentrations. Hydrothermal reactions were carried out at 90°C for 4 h. The structural and optical properties of the samples were studied. The grown ZnO nanorods were used for photo
catalytic degradation of methylene blue dye in the presence of UV irradiation. The efficiency of dye degradation was reported.

Photo catalysis is a light induced catalytic process whereby photo generated electron-hole pairs in a semiconductor undergoes redox reactions with molecules adsorbed onto the surface, thereby breaking them into smaller fragments [19]. Hydrothermally grown ZnO nanorods have inherent crystalline defects primarily due to oxygen vacancies that enhance optical absorption in the UV and visible spectrum, opening up possibilities for photo catalysis [20].

In the present work,

a) The chemical bath deposition method (CBD) was used to prepare ZnO seed layers.
b) Using hydrothermal method ZnO nanorods were grown.
c) Structural, morphological and optical properties of the deposited ZnO nanorods were studied. The growth layer concentration and the annealing temperature were optimized to 1:10 and 500°C respectively.
d) The photo catalytic activity of undoped ZnO nanorods was carried out on methylene blue by varying irradiation time and film area.
e) Aluminium, strontium and lithium were doped with ZnO nanorods and their photo catalytic properties were studied. The respective degradation efficiencies were reported.

ZnO nanorods prepared on the glass slides offer higher surface to volume ratio compared to nano particle thin films, allowing higher adsorption of the target molecules and hence improve photo catalytic activity [21]. CBD method was used to prepare the ZnO seed layers. All the reagents (Merck 99.99%) used in the experiment were analytically pure and they were used without further purification. 0.1 mol of zinc acetate was dissolved into 10ml of ethanol and 0.25ml of distilled water was introduced drop by drop through syringe. This solution was stirred continuously for 2 hours at room temperature for obtaining clear homogenous solution. The stirred solution was taken in a beaker and the well cleaned glass substrates were dipped in the solution for 5 times at regular intervals at room temperature using automatic dip coating system (Holmarc - HO-
Then this 5 layer films were annealed in a furnace at a temperature of 200℃ for 1 hour.

Hydrothermal synthesis of ZnO nanorods has several advantages for photocatalytic applications, including low reaction temperature, low cost, high yield, catalyst-free growth and is environmentally benign [22]. Hydrothermal treatments were carried out by suspending the ZnO seed coated glass substrates in upside down position in a glass beaker filled with aqueous solution 0.02 mol of zinc nitrate and 0.1 mol of hexamethylenetetramine (HMT) on 1:5 molar concentration. The same treatment was carried out for 1:10 and 1:15 molar concentrations also. The above solution was mixed through magnetic stirrer for 2 hours. During the growth process the solution was heated with a hot air oven and maintained at 90℃ for 4 hours. At the end of the growth period, the substrates were taken from the solution and immediately rinsed with de-ionized water to remove the residuals from the surface and dried in air at room temperature. Then the above films were annealed in muffle furnace at different temperatures of 300℃, 400℃ and 500℃ for 1 hour.

Photo catalytic activity was carried out in a specially designed reactor. The Hydrothermally grown ZnO nanorods were used as catalysts. 0.5 mol of methylene blue dye was taken in a beaker and ZnO nanorods were suspended into the beaker and treated with UV lamp by varying irradiation time and area of catalyst.

The crystal structure of ZnO nanorods were investigated by X-ray diffractometer (XPERT-PRO). The XRD patterns of the ZnO nanorod arrays corresponding to the different growth layer concentrations (1:5, 1:10 and 1:15) and different annealing temperatures (300℃, 400℃ and 500℃) were studied [23]. From the XRD results it was observed that at growth concentration of 1:10 and at the annealing temperature of 500℃, a very strong (002) diffraction peak and a very weak (100) and (101) peaks were observed. The detected (h k l) peaks were at 2θ values of 31.7647°, 34.4227° and 36.2520° corresponding to the lattice planes (100), (002) and (101) respectively. They are in good agreement with the standard JCPDS 036-1451 card for hexagonal wurtzite ZnO. The intensity of the peak was found to vary with the different growth layer
concentrations. C-axis orientation was observed for ZnO nanorods grown on 1:10 concentration and annealed at 500°C.

The effective surface area available for photo catalytic dye adsorption is a function of thickness, length and density of the nanorods covering the substrate. The average exposed surface area can be approximated using scanning electron microscope (SEM) [24]. The Surface morphology of ZnO nano rods were studied by SEM (HITACHI S-4800). The SEM images of ZnO nano rods grown under different growth layer concentrations (1:5, 1:10 and 1:15) and different annealing temperatures (300°C, 400°C and 500°C) were studied. ZnO nano rods having different orientations and sizes were formed under different molar ratios and annealing temperatures. The nanorods grown at 1:10 molar ratio and annealed at 500°C showed vertical alignment resembling the XRD patterns.

The optical absorption in the UV region and corresponding photo efficiency influences the use of ZnO nanorods for photo catalytic activities [25]. The absorption and transmittance spectra of grown ZnO nanorods were recorded by UV–Vis spectrophotometer (JASCO Corp., V-570) at room temperature. It was observed that as annealing temperature increases the optical absorption edge was shifted to a higher wavelength. The absorbance was found to increase considerably as the growth solution concentration increases from 1:5 to 1:15. The optical band gap of ZnO films was found to decrease with the increase in annealing temperature. The decrease in band gap of ZnO films may be attributed to the improvement in the crystalline quality of the films and increase in grain size. The transmittance spectra was within the visible range nearer to infrared wavelength region, which reveals the superior optical properties in the ZnO thin films produced by chemical bath deposition method. A slight decrease in average transmission was observed with the increase of annealing temperature and was attributed to the increase of surface roughness.

The room temperature photoluminescence (PL) spectra of the grown ZnO nano rods were recorded using photoluminescence spectrophotometer (HORBIA JOBIN YVON-Fluorolog) at an excitation wavelength of 350 nm. The obtained PL results
revealed that the visible PL emission is enhanced while the UV emission is suppressed as growth solution concentration increases and particularly at the concentration of 1:10. This is due to large competition from the defect emission and increase in both the oxygen vacancies and zinc interstitials.

The Photo catalytic degradation was carried out in a specially designed reactor in which the light source was 8W UV lamp (Philips TUV-08). The photo degradation was carried out on methelene blue, the commonly used reactive dye using undoped ZnO nanorods as catalysts, by varying the irradiation time and area of the catalyst. The effective surface area (adsorbed amount of target molecules) and the diffusivity are important indices to gauge photo catalytic activity [9]. The UV studies were recorded by UV–Vis spectrophotometer (JASCO Corp., V-570). For the degradation experiments, fixed amount of methelene blue dye was taken in a beaker and undoped ZnO nanorods were suspended inside the beaker. The beaker was subjected to irradiation under UV light kept at a distance of 15cm for fixed interval of time. The degradation efficiency was found to increase from 42%, 47% to 74% respectively for the irradiation time of 1 hour, 2 hour and 3 hour. It was also found that the degradation efficiency increases from 43% to 75% as the area of catalyst (ZnO nanorods film) was increased from 1cm$^2$ to 2cm$^2$.

The ZnO nanorods were doped with aluminium, strontium and lithium and their photo catalytic activity was carried out on methelene blue with the same experimental conditions. The respective degradation efficiencies were reported. Doping of metal oxides or transition metals creates quasi-stable energy states within the band gap (surface defects) thereby affecting the photo catalytic properties [26]. For Al doped ZnO nanorods the degradation efficiency was found to increase from 28%, 32% to 34.2% respectively for the irradiation time of 1 hour, 2 hour and 3 hour. It was also found that the degradation efficiency increases from 32% to 37% as the area of catalyst was increased from 1cm$^2$ to 2cm$^2$. For Sr doped ZnO nanorods the degradation efficiency was found to increase from 27%, 32% to 42% respectively for the irradiation time of 1 hour, 2 hour and 3 hour. It was also found that the degradation efficiency increases from 30.5% to 44.7% as the area of catalyst was increased from 1cm$^2$ to 2cm$^2$. For Li doped ZnO nanorods the degradation
efficiency was found to increase from 25.2%, 28% to 34.2% respectively for the irradiation time of 1 hour, 2 hour and 3 hour. It was also found that the degradation efficiency increases from 25% to 30.5% as the area of catalyst was increased from 1 cm$^2$ to 2 cm$^2$.

References