Investigation of Structure, Morphology, Optical And Luminescent Properties of Hydrothermally Grown Zno Nanorods for Photocatalytic Applications

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Abstract- *The research paper reports on a systematic study of structural and optical properties of ZnO nano rods for Photocatalytic Applications. Zinc oxide (ZnO) thin films were deposited on an ordinary glass substrate by dip coating technique and grown by hydrothermal method from aqueous solution of Zinc Nitrate and hexamethylenetetramine with seed layer of Zinc acetate dihydrate at low temperature of 100°C. The prepared ZnO nano rods were annealed at 500°C temperature in air atmosphere. Zinc acetate dihydrate and ethanol were used as a starting material and solvent respectively. The crystal structure and orientation of the ZnO nano rods were investigated by X-ray diffraction (XRD) patterns. The surface morphology of the ZnO thin films was investigated by Scanning Electron Microscopy (SEM). The optical absorbance and transmittance measurements were recorded by using a UV visible spectrophotometer and photoluminescence (PL) spectra. An optimized hydrothermally grown ZnO nano rods were prepared and investigated using sol-gel dip coating method for Photocatalytic Applications.*

Keywords- ZnO Nano Rods, Sol-Gel Method, Dip Coating, Hydrothermal, Photocatalysis, Thin Films

I. INTRODUCTION

Zinc oxide (ZnO) is a unique material with a direct band gap (3.37eV) and large exciton binding energy of 60 meV, which makes the exciton state stable even at room temperature. ZnO has been widely used in near-UV emission, gas sensors, transparent conductor, thin film transistors and piezoelectric applications.

In this work we have used glass slides as the support for ZnO nano rod photocatalysts. When affixed on to a support, ZnO nano rods offer higher surface to volume ratio compared to nano particulate films, allowing higher adsorption of the target molecules. The ZnO nano rods were fabricated by dip coating method and the variation in annealing temperatures for controlling the growth rate of ZnO nano rod was made. ZnO nano rods were grown by a hydrothermal process at low growth temperature of 100°C and were annealed at 500°C temperature for 1 hour. The structural and optical properties of ZnO nano rods were systematically investigated. Hydrothermal growth of high quality ZnO nano rods perpendicularly oriented on glass substrates was reported. These high quality ZnO nano rods can be applied as catalyst for many applications.

Our work provides controllable structural and optical properties of ZnO nano rods prepared on ZnO thin films with different annealing conditions were systematically studied. Our investigations indicated that the thin film annealed at the temperature of 500°C amorphous, but the Nano rods were high quality single crystals growing along the various directions with a high consistent orientation perpendicular to the substrates. We brief the experiments including preparation and annealing treatment of ZnO sol-gel thin films and the growth of thereon ZnO Nano rods.

II. EXPERIMENTAL DETAILS

The ZnO nano rods were prepared from zinc nitrate in a neutral aqueous solution under hydrothermal conditions.

The procedure consists of two steps:

- ZnO Seed layer thin film: Sol-Gel Method by dip coating technique.
- ZnO Growth Layer thin film: Hydrothermal Method of ZnO nano rods in aqueous solution.

1. ZnO Seed layer Thin Film: Sol-Gel Method

The ZnO thin films served as the seed layers were deposited on glass substrates by a sol-gel method. A coating solution was prepared by dissolving Zinc acetate dihydrate [$(CH_3COO)_2$ Zn.2 H_2O] and equivalent 20 ml Ethanol [C2H5OH] in 0.25 mol of de-ionized water. The concentration of Zinc acetate was 0.1mol. The resulting solution was then stirred 2 hours at room temperature to yield a homogeneous and stable colloid solution, which served as the ZnO seed layer thin films. Then the solution was coated onto glass substrates by dipping method. Well cleaned glass substrates were immersed in the seed ZnO solution for 1min dip and 5mins dry by dip coating method and taken out. All the glass substrates were dipped and dried 5 times at room temperature to get desired film thickness. Then the 5-layer films were annealed in a furnace at the temperature 200°C for 1 hour. Fig.1shows the flow diagram of the ZnO Seed Layer Nano Rods Thin Film prepared from sol gel process using the dip-coating method.

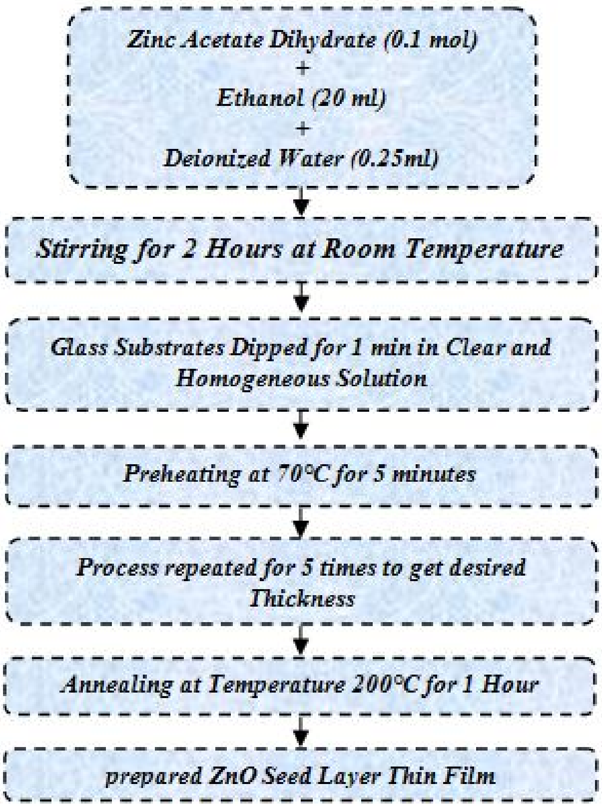


Fig.1 Flow chart depicting the preparation of ZnO seed layer thin film

2. ZnO Growth Layer Thin Film: Hydrothermal Method

After uniformly coating the glass substrates with ZnO thin films, hydrothermal growth of ZnO Nano rod was achieved by suspending these ZnO seed-coated glass substrates upside-down in a glass beaker filled with aqueous solution of 0.02 mol of Zinc Nitrate dihydrate $[Zn(NO_3)_2.6H_2O]$ and 0.2 mol of Hexamethylene tetramine (HMT) $[C_6H_{12}N_4]$. During the growth, the glass beaker was heated with a laboratory oven and maintained at temperature 100°C for 4 hours. At the end of the growth period, the substrates were removed from the solution, then immediately rinsed with de-ionized water to remove any residual salt from the surface, and dried in air at room temperature. Then the ZnO grown films were annealed in a furnace at the temperature 500°C for 1 hour. Here we report the effect of three different precursor concentrations on the grown ZnO Nano rods with constant annealing temperature. Concentrations of 0.02mol of Zinc Nitrate and 0.2 mol hexamethylene tetramine (HMT) were taken in the ratio of 1:10.

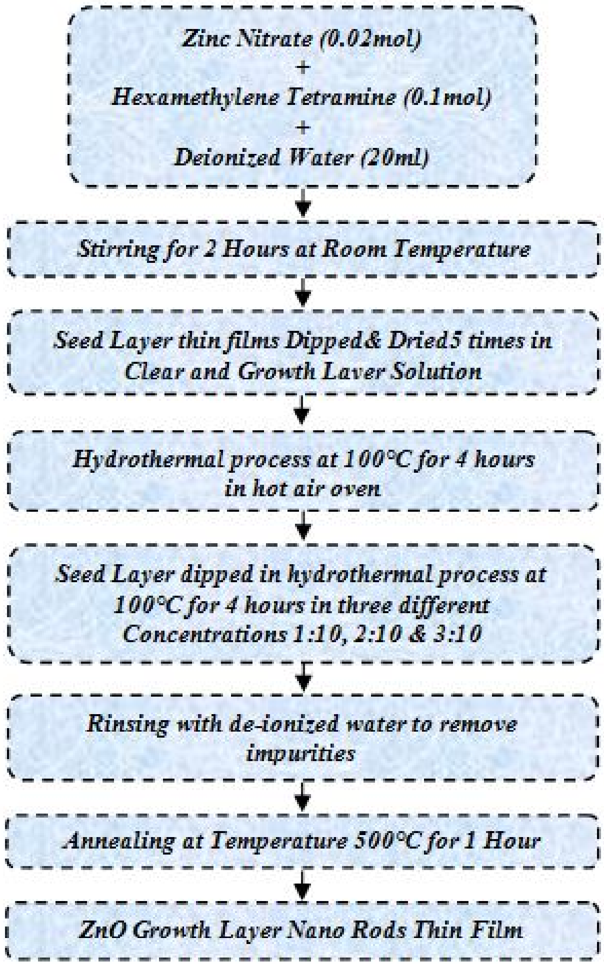


Fig.2 Flow chart depicting the preparation of ZnO growth layer Nano rods thin film

The flow diagram shown in Fig.2 depicts the detailed preparation procedure of ZnO nano rods. The other two ratios were 2:10 and 3:10. ZnO Nano rods were grown in above three concentrations, annealed at same temperature of 500°C for 1 hour. The properties of grown ZnO nano rods were investigated by X-ray diffractometer (XRD). The surface morphology of the ZnO thin films was investigated by Scanning Electron Microscopy (SEM). The optical absorbance and transmittance measurements were recorded by using a UV visible spectrophotometer and photoluminescence (PL) spectra.

III. RESULTS AND DISCUSSION

1. Structural Analysis

XRD patterns of the ZnO Nano rod samples are shown in Fig.3. It reveals that the well-aligned Nano rods have a hexagonal wurtzite crystal structure with a c-axis (002) preferential orientation.

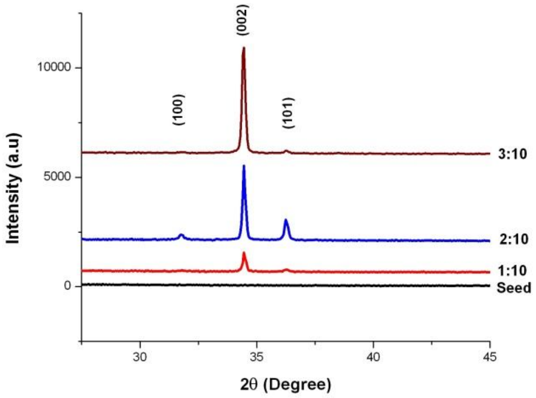
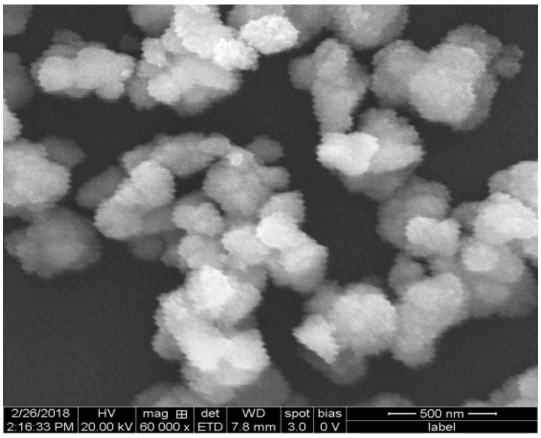


Fig.3 XRD pattern of ZnO growth layers on different growth solution concentrations at 500°C with Seed Layer

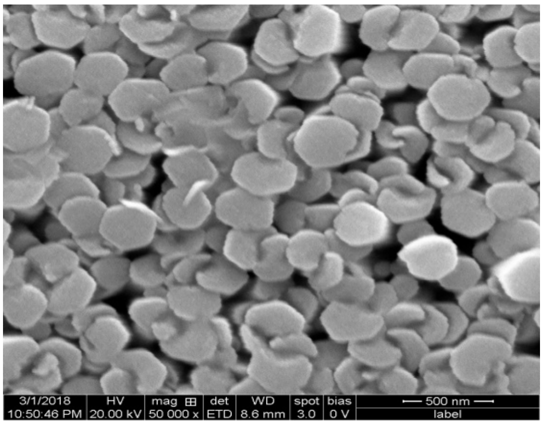
The XRD pattern of the growth concentration of 1:10 and 2:10 shows typical polycrystalline characteristics with relatively comparable intensity for the (100), (002) and (101) peaks. When concentration of 1:10 and 2:10 is compared, the 2:10 concentration is better than 1:10 concentration, which is seen in the XRD pattern, where (002) peak is stronger. The XRD pattern 3:10 growth concentration is displays only the (002) diffraction peak of the ZnO, indicating the good orientation in the c-axis direction. The strong and narrow diffraction peaks indicate that the material has a good crystalline and size. From the above XRD patterns it is clearly seen that, as the growth concentration increases the diffraction peaks were oriented strongly along the (002) peak.

2. Morphological Analysis

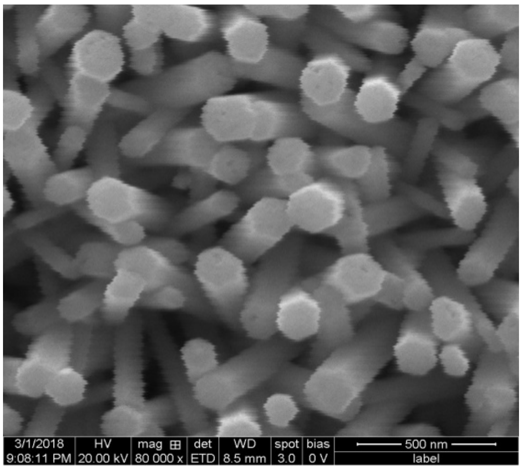
Fig.4 (a-d) shows the SEM images of films as prepared and different growth layer solution concentrations annealed at 500°C temperature. Fig.4 (a,b,c,d) show the SEM images of films of Seed layer and different growth layer concentrations of 1:10, 2:10 and 3:10 respectively. They show the dense arrays of hexagonal ZnO growth layers having different diameters that are formed under different molar ratios. In Fig.4a, the as prepared film shows that rods grown in cloudy like pattern. It is not clearly seen that from Fig.4b to 4d as different concentrations, the ZnO nano rods are oriented towards the vertical direction, which resembles the XRD pattern. The densities of the rods grown are decreased and diameter of rod size is increased as the ratio increases. In Fig.(b), (c), & (d)molar ratio films show that layers grown in all directions. It is clearly seen that from Fig.4b and 4c molar ratio increases i.e., 2:10 and 3:10, the ZnO growth layers are oriented towards the vertical direction, which shows the c-axis orientation. The effective surface area available for photo catalytic dye adsorption is a function of thickness, length and density of the nano rods covering the substrates.



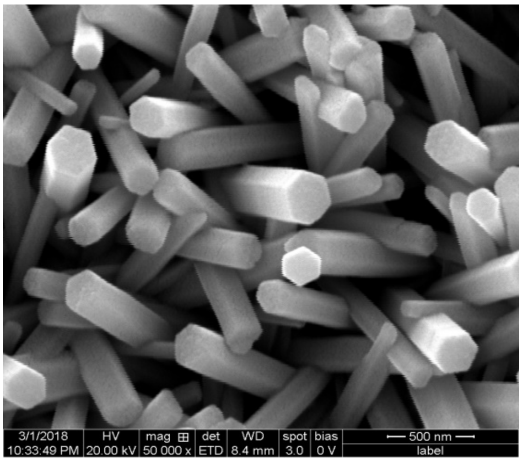
(a) As prepared ZnO nano rod (Seed)



(b) Growth solution concentration 1:10



(c) Growth solution concentration 2:10

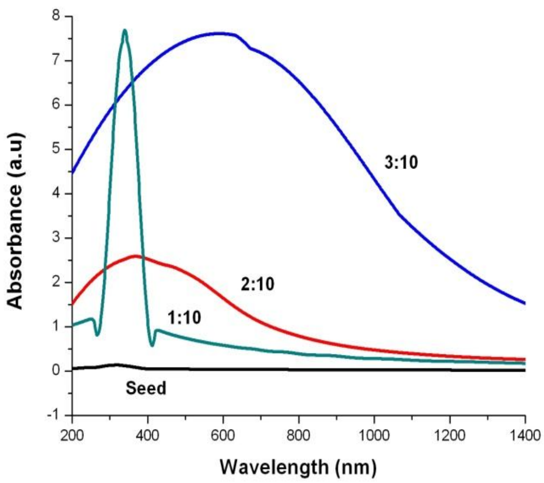


(d) Growth solution concentration 3:10

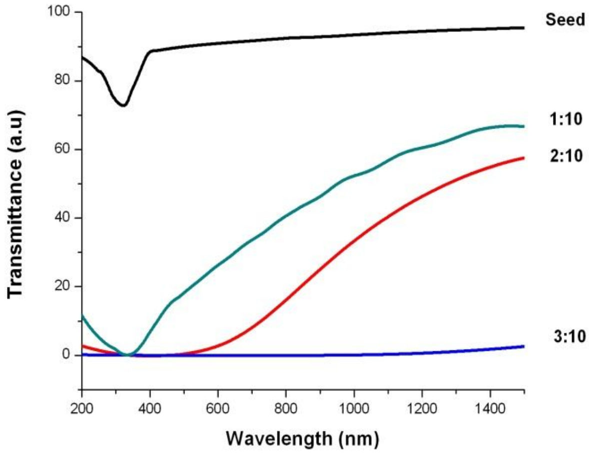
Fig.4 SEM images of ZnO nano rods on different growth solution concentrations annealed at 500°C

3. Optical Analysis

The Optical properties of ZnO Nano rods are important for many of their technological applications. In most cases the UV-Vis spectra of ZnO comprised of Absorption and Transmittance and the relationship between the two depends strongly on the preparation method and post-preparation treatment. The UV spectra in ZnO Nano rods are well accepted as the near-band-edge emission. The optical absorption spectrum is shown in Fig.5 (a) is clearly indicates that, as growth solution concentration increases the optical absorption edge shift to a higher wavelength. The intensity of the absorption spectra increases considerably as growth solution concentration increases from 1:10 to 3:10. It is well known that the optical absorption determines the optical band gap and ZnO films have a direct band gap. The optical band gap of ZnO films was found to decrease as growth solution concentration increases from 1:10, 2:10 and 3:10 respectively.



(a) Absorption



(b) Transmittance

Fig.5 Absorption and Transmittance spectra at three different growth solution concentrations with Seed Layer

The decrease in band gap of ZnO films may be attributed to the improvement in the crystalline quality of the films and increase of grain size. Fig.5 (b) shows the optical transmittance spectra from samples with three different growth solution mol concentrations of 1:10, 2:10 and 3:10, annealed at constant temperature of 500°C for 1 hour, which was obtained on a spectrophotometer. A slight decrease in average transmission was observed with the increase of growth layer molar concentration and was attributed to the different of surface roughness. The optical band gap of ZnO films was found to increase as growth solution concentration increases from 1:10, 2:10 and 3:10 respectively The results indicated high optical quality ZnO Nano rods were successfully achieved via this low temperature chemical approach.

4. Photo Luminescence (PL) Analysis

The Room temperature Photoluminescence spectra of ZnO samples obtained with an excitation wavelength of 350nm for three different solution concentrations annealing at 500°C temperature and as-prepared is shown in the fig.6. The Ultraviolet (UV) emission peak in the range dominates all the PL spectra, the only difference being the relative intensity of peaks.

The intensity of this broad visible PL emission is highly sensitive to the environment and mainly depends on the surface to volume ratio of the nano particles. The obtained PL results of the samples indicate that the visible PL emission is enhanced while the UV emission is suppressed as growth layer solution concentration increases and particularly 3;10 ratio annealing at 500°C, due to large competition from the defect emission and increase in both the oxygen vacancies and zinc interstitials.

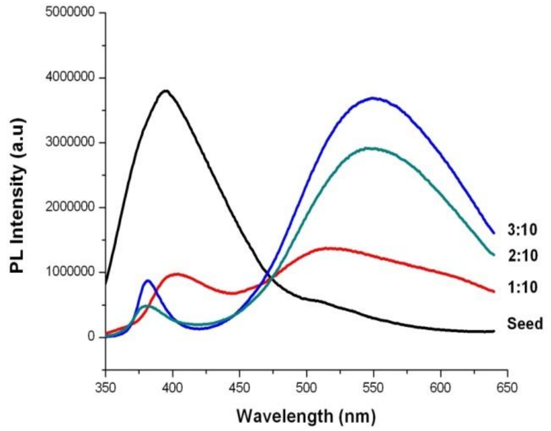


Fig.6 Room temperature Photoluminescence spectra obtained at different growth solution concentrations annealed at 500°C with Seed Layer

IV. CONCLUSION

ZnO nano rods were synthesized by hydrothermal method at low growth temperature of 100°C and their structural, morphological and optical properties were studied. The results illuminate that the change in growth solution concentration, play crucial role in the growth rate, size and density of the layers. From the results, it was clearly observed that, at 3:10 growth concentration at 500°C annealing temperature, ZnO nano rods with good structural, morphological and optical properties can be grown.

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