Mechanochemical Synthesis, Characterization and Photocatalytical Degradation of Methyl Orange by Nano-ZnO

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Abstract

Nanosized ZnO particle were synthesized by using a mechanochemical method. The Morphological, Compositional and Structural properties of the ZnO thick films were performed by Scanning electron microscopy (SEM), Energy Dispersive Spectroscopy (EDAX) and XRD technique respectively. Chemical composition of nano ZnO film samples changes with firing temperature showing non-stoichiometric behaviours. XRD study indicated the formation of polycrystalline ZnO films with hexagonal wurtzite structure. The effect of catalyst loading, pH value, and initial concentration of methyl orange on the photocatalytic degradation efficiency using ZnO particle as photocatalyst were discussed.

Keywords:Degradation, Methyl orange, Photocatalysis, Zinc oxide.

INTRODUCTION

Zinc oxide is widely used in number of application like photocatalysis[1], gas sensor[2], varistors[3], low voltage phosphor material[4] and so on. In order to realize the universal application of nanomaterials, the key is to devise simple and efficient methods for preparing nonmaterial on a large scale at low cost[5]. ZnO nanoparticles can be prepared on a large scale at low cost by simple solution-based synthesis methods, such as chemical precipitation[6], sol–gel[7,] and solvothermal, hydrothermal reaction[8]. Number of other methods such as photochemical, electrochemical and chemical reduction, microwave processing[9], gamma irradiation[10], ion irradiation[11] and plasma processing, radiolysis, ultra sound processing also helps in synthesizing nanoparticles.

ZnO is a II-VI semiconductor material with a wide direct band gap (3.37 eV) and relatively high exciton binding energy (60 meV) at room temperature. It has attracted considerable attention with respect to degradation of various pollutants such as acid red 18[12], 4-nitrophenol[13], acridine orange[14], methyl orange)[15], and so on, due to its being relatively cheap, chemical stability and high photocatalytic efficiency[16]**.**

Methyl orange (MO) is an azo dye and has been widely used in textiles, foodstuffs, paper and leather industries. However, the release of MO and its products in the environment cause serious pollution problems. The photocatalytic treatment of waste waster containing dyes has also been well documented [17,18]. ZnO has attracted much attention with respect to the degradation of various pollutants because of its high photosensitivity. Researchers have highlighted the performance of ZnO on degradation of some organic compounds[19, 20]. It is well known fact, the highly reactive $OH^{\bullet}$ radicals and electron holes are generated on the surface of photocatalyst under the irradiation with UV light. Therefore, the surface characteristic of ZnO determined by the different methods will influence this property as well as the final degradation efficiency. The particle size of photocatalyst is one of the most important factors. The aim of the study is to optimize the preparation of ZnO nano particle as a photocatalyst. The photocatalytic activities were evaluated using methyl orange (Scheme 1) as a model organic compound.

MATERIALS AND METHODS:

Preparation of nano sized photocatalyst

ZnO Oxide was synthesized using a mechanochemical and conventional solide- state method. All

the chemicals used for the preparation were of analytical grade. It includes ZnO, Poly vinyl alcohol (1%) and acetone. All the solutions were prepared in Millipore water obtained from Millipore water system for the preparation of ZnO nanoparticle. Weighted 5 g of ZnO powder and mixed thoroughly in an aceton medium using agate mortar pestle for 2 hr and dry it. The powder of ZnO has been taken in 100 ml beaker and adds 3-4 mL 1% poly vinyl alcohol. The mixture is sticky. Dry the mixture with a natural process. This mixture is added with 150 mL Millipore water. The solution was allowed to centrifuge in presence of water and acetone to remove impurities. The process of centrifuging was repeated three- four times to remove most of the impurities for the solution and allowed to dry at room temperature. The reaction was carried out at 100^0C for 2 hr in a muffle furnace. The dried powder of ZnO is used for the characterization by XRD, SEM Energy dispersive spectroscopy (EDX) and photocatalytic degradation of methyl orange.

RESULT AND DISCUSSIONS:

X-ray diffraction:

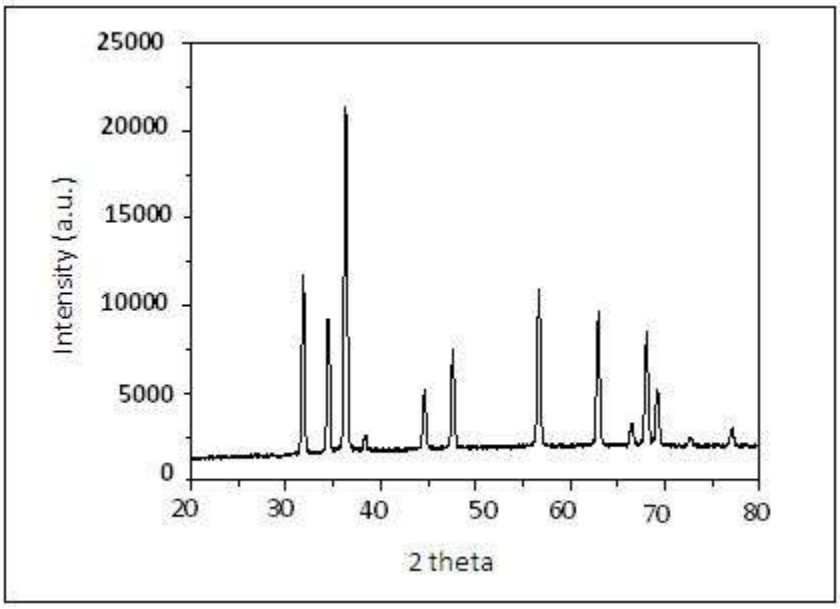


Figure1. XRD pattern of ZnO nanoparticle

In order to understand the structural properties of ZnO sample fired at different temperature in air atmosphere, the X-ray diffraction study was undertaken. X-Ray diffraction analysis of ZnO samples was carried out in the range 20- 80(2θ) range using CuKα radiation. Figure1. shows an XRD pattern of ZnO sample plotted in the range 20-80(2θ) versus intensity having several peaks of ZnO indicating random orientation for the hexagonal wurtzite nature and measured interplaner distance agreed with the value reported for ZnO in literature. The observed peak matches well with the reported JCPDS data of Number 21-1486 matches with calculated values, confirming the hexagonal wurtzite structre[21]. The higher peak intensities of an XRD pattern is due to the better crystallinity and bigger grain size. This clearly indicates that the structure of ZnO film is polycrystalline in nature. Besides except ZnO peaks, no other impurity peak is seen, suggesting formation of the single phasic ZnO. The average crystallite size as per the calculations was found to be 80-100 nm (±2 nm).

SEM analysis:

The scanning electron microscopy is useful technique to observe surface morphology of deposited films. SEM images shows that the structure like porous and wafer type. This is because of

porosity of the film as deposited at room temperature. Figure2. shows SEM images of nanostructure ZnO thick film fired at 500^{o}Cin the air. Microstructural characterization was carried out by using scanning electron microscopy. SEM indicated rod type nanostructure with porosity. However some residual, intragranular porosity was seen. The film fired at 500^{o}C has good adhesion. Therefore it is used for gas sensing. The surface morphology (SEM) of ZnO nanoparticle, which reveals the particles size was found to be about 10 nm with hexagonal shape.

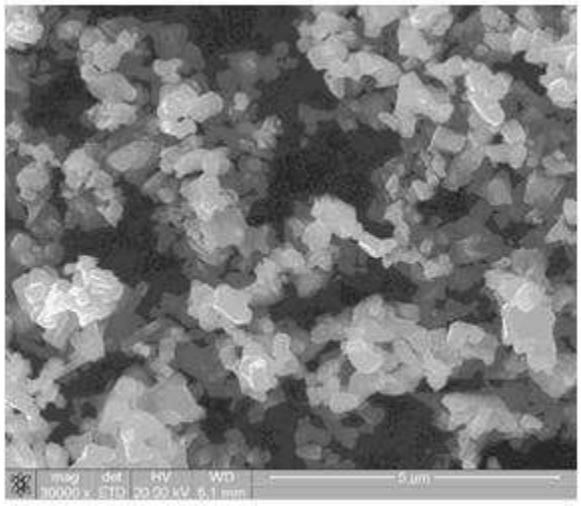


Figure2. SEM image of ZnO nanoparticle

Elemental Analysis:

The composition of ZnO nanoparticle fired at different temperature was analyzed by energy dispersive spectrometer (6360LA) (EDX).The EDAX was recorded in the Binding energy region between 0-20 KeV was shown in Figure3. The spectrum peak reveals the presence of Zn and O at 8.50 and 0.5 KeV respectively, which confirms the presence of Zn and O in the film. Table1. Shows the composition of the film fired at different temperature. The EDAX spectrum showed the presence of Zn and oxygen. From the analysis it was found that the ZnO films are nonstoichiometric. The deficiency or excess of any type of atom in the crystal results in a distorted band structure, with a corresponding increase in conductivity .The oxygen, of course, evolves as an electrically neutral substance so that it is associated with each excess tin ion in the crystal; there will be two electrons that remain trapped in the solid material, thus leading to nonstoichiometry in the solid. This leads to the formation of the n-type semiconductor[22].

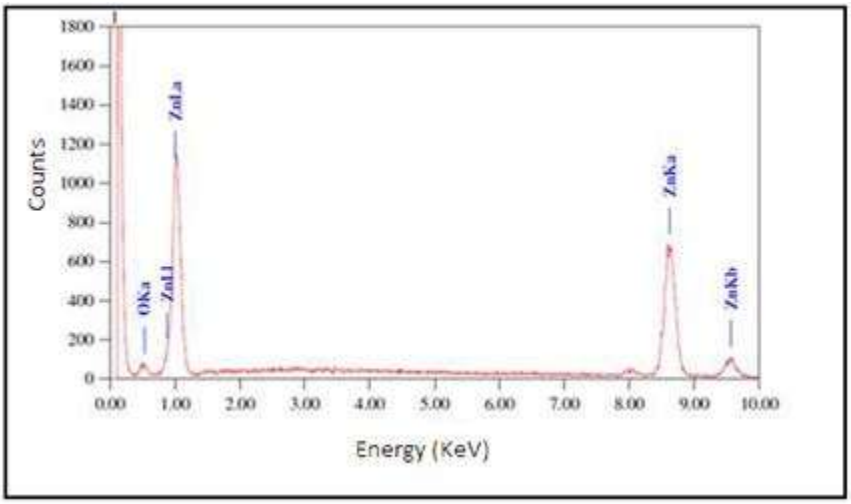


Figure3. EDAX Spectrum of ZnO

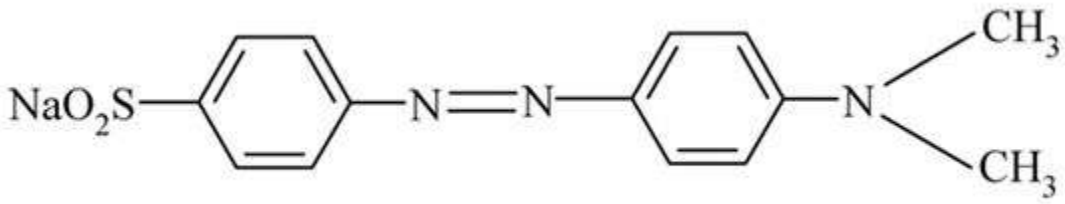
Table1. Composition of the sample

Element	At. Wt. %	Mass %
O	4.25	1.08
Zn	95.75	98.92
Total	100	100

Photocatalytic activity measurements:

The photodegradation efficiency with a definite concentration of methyl orange in aqueous solution under the illumination of UV was carried out. The photocatalytic activity of ZnO nanoparticle were evaluated reliably. The methyl orange is A.R grade and was used as supplied. The photocatalytic reactor consist of two parts: a 100 mL Pyrex glass bottle and a 125W high pressure Hg lamp with maximum emission at about 365 nm, which was positioned parallel to Pyrex glass bottle. The distance between the top of Pyrex glass bottle and the UV lamp was 10 cm and the light intensity was about 4.0×10^{-3} W/cm^2. All the experiments were carried out at temperature 27 $\pm$ 1°C. Reaction suspensions were prepared by adding photocatalyst powder into 100 mL methyl orange solutions. The suspensions were magnetically stirred in dark for about 30 minutes to ensure adsorption equilibrium prior to the UV-irradiation. The suspensions containing methyl orange and photocatalysts were then irradiated under UV light with continuous stirring. The degradation of the methyl orange with time was monitored by using UV- Visible spectrophotometer, Shimadzu (UV-160 PC Japan) in the range of 250 - 600 nm.

For investing the effect of pH on the photodegradation efficiency, NaOH (1mol L^{-1}) and HCl (1 mol L^{-1}) solutions were used to adjust the pH values of the pure dye solutions before the catalyst addition. Analytical samples were drawn from the reaction suspensions after various reaction times and centrifugated at 8000 rpm for 15 min. The photodegradation efficiency was monitored by recording the absorbance for the solutions in the range between 250-600 nm with UV-Visible spectrophotometer. The decolorization efficiency as a function of time was calculated by the absorbance values of the original and analytical samples. ZnO nanoparticle annealed at 100°C temperature were used for all the photocatalytic experiments. The molecular structure of methyl orange is shown in scheme1.



It is well known that ZnO is an important photocatalyst and it has been widely used in solar cells and for the treatment of wastewater. Its photocatalytic process is based on the generation of electron–hole pairs by means of band-gap energy, which can give rise to redox reactions with species adsorbed on the surface of the catalysts[23]. In the photocatalytic process, generally, the operated matter is considered to be the hydroxyl free radicals ($^{\bullet}OH$), which originate from the oxidation of OH^- or H_2O by the photogenerated electron–hole pairs in the presence of oxygen. They are strong oxidants and can oxidize the coloured groups of the organic dyes to lead the fading of the colorisation. The possible formation process of hydroxyl free radicals in the system containing ZnO as a nanorods is described as follows[24].

$$ZnO + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \quad (2)$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \quad (3)$$

The above experiments proved that ZnO nanoparticles possess the best photocatalytic degradation ability for MO, which was completely degraded after irradiation for 80 minutes.

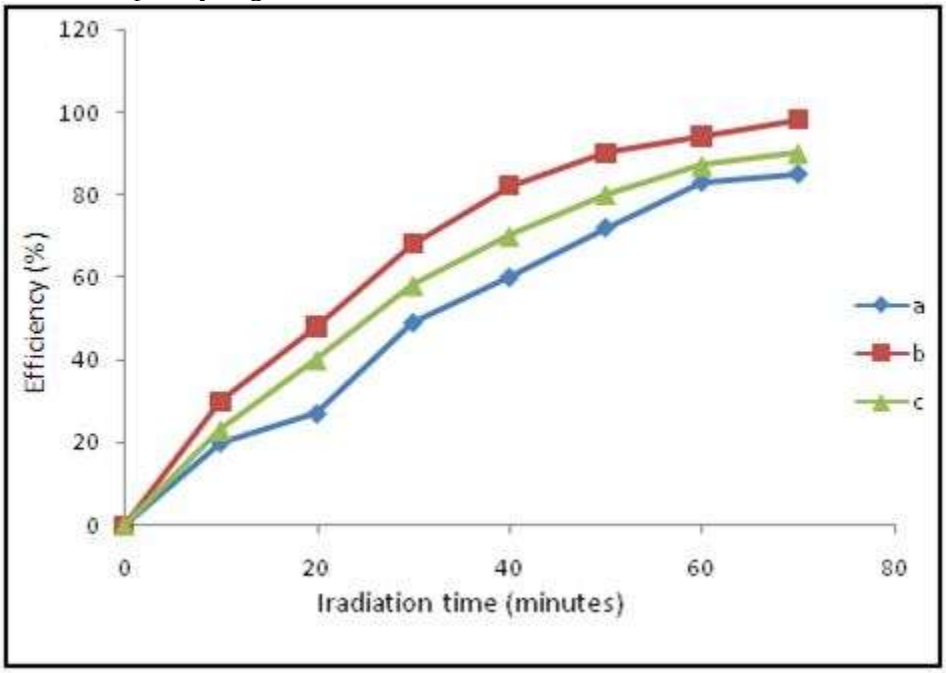


Figure4. Effect of catalyst concentration on the photodegradation efficiency at pH 7.0: (a) 0.1 g dm^3(b) 0.2 g dm^3 (c) 0.3 g dm^3.

To investigate the effect of catalyst loading on the final decolorization efficiency, a series of experiments were carried out by varying the catalyst amount from 0.1g/dm^3 to 0.3g/dm^3 in the solution with 20 mg/dm^3 dye concentration. The rate of degradation is illustrated in Figure 4. (a), (b) and (c). It is demonstrated that the decolorization efficiency was increases with the amount of catalyst loading. From the photocatalytic degradation experiments, the 0.2g/dm^3 catalyst loading was suitable, which shows

almost 95% degradation efficiency it may be due to large surface area and proper adsorption of dye solution on the catalyst surface.

The effect of pH values on the degradation efficiency were studied in the pH range from 3-12 the catalyst loading amount at 0.2g/ dm^3 and initial dye concentration is
20 mg/dm^3. Figure5. (a), (b), (c), (d) and (e) demonstrate the results of decolorization efficiency for 80 minute light illumination at different pH values. It can be seen a fast increase in the degradation of methyl orange with increase in the pH value from 3 to 10 followed by the slight decrease at pH 12. As an amphoteric nature of oxide, ZnO can be dissolved both at acidic and alkaline environment. In the present work, at the lower pH value (pH 3), since the dissolution of ZnO, the activity of catalyst is reduced greatly, which induces the depressing of photodegradation process[25].

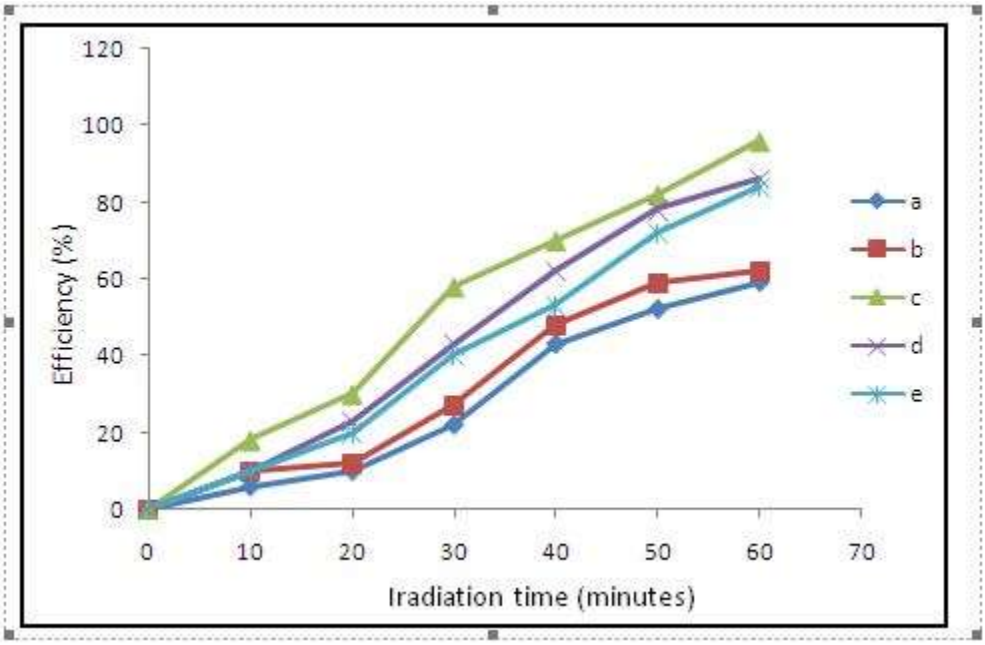


Figure5. Effect of pH values on the photodegradation efficiency:
(a) pH 3, (b) pH 5, (c) pH 7, (d)pH 10, and (e) pH 12.

In the pH range from 5-10, the surface characteristic of ZnO nanoparticle was the limiting factor for pH values can change its surface charge property. It has been reported that the pH of zero point charge for ZnO is 9.0[26]. When pH value is higher than 10, the ZnO surfaces is negatively charged by adsorbing OH^- ions, which favours the formation of hydroxyl radicals. However, when pH value is lower than 5, the ZnO surface is preferentially covered by the dye molecules. Therefore, with increase of pH value, which provides higher OH^- ions to form more hydroxyl radicals, consequently enhancing the photodegradation efficiency. On the other hand, with the increase in pH values, the electrostatic repulsion between the methyl orange anion and oxide surface gradually increases[27]. In that case, the slow diffusion of surface-generated $OH^\bullet$ towards the double layer at the low concentration of methyl orange anion will make the photodegradation process of methyl orange slower than direct charge transfer[28]. For the competition of the two factors, the highest decolorization efficiency was obtained at pH-7. However, at pH- 12, the decolorization efficiency was comparatively slow. Therefore degradation efficiency of MO at pH 7 is comparatively higher than reported[29].

CONCLUSIONS:

We have developed a rapid, environment friendly and energy saving mechanochemical method for the synthesis of photocatalylic ZnO nanorods. The mechanochemical method is very simple to

implement, which can be easily extended for the preparation of other oxide nanoparticles also. It was found that ZnO nanoparticle prepared by mechanochemical method plays key role in the photocatalytic performance through studying degradation efficiency. The shape of particle was wurtzite structure. As the annealing temperature increases the particle size and crystallinity increases. The photocatalytic results indicated that the catalyst loading and pH values affected the degradation efficiency of ZnO nanoparticle. Obviously, we learned that the photodegradation efficiency might be increased with the increase of catalyst loading. The photocatalytic decomposition of methyl orange was most efficient at pH 7 and 0.2g/dm^3 loading of catalyst within 80 minutes. The degradation efficiency obtained for Methyl Orange was high than the reported.

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