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Synthesis of ZnO Nanomaterial by Precipitation Method and its Characterization

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Abstract

Nanosized zinc oxide (ZnO) powders were prepared by precipitation method from zinc acetate powder and sodium carbonate. The ZnO nanopowders were characterized by X-ray diffraction, UV-Visible spectrometry, transmission electron microscope and FTIR. The X-ray diffraction analysis of the sample showed the formation of nanopowders with wurtzite ZnO structure. Diffraction peaks are indexed to the crystalline hexagonal phase of the ZnO nanomaterial, with lattice constants of a = 3.264Å, d=5.219Å. The UV-visible absorption band of the ZnO nanoparticles have been shows a red shift due to the decrease in the band gap energy of the particle. The maximum absorption of the nanoparticles shows at 380nm and band gap energy was calculated to be 3.26 eV. The photocatalytic activities of ZnO powders were evaluated by measuring the degradation of Phenol Red (PR) in water under the UV region.

Keywords: Co-precipitation method, Nanomaterial, Phenol Red, Photocatalysis.

Introduction:

Zinc oxide which is n-type semiconductor material, band gap group II-VI has received great deal of attention in research and various fields[1]. Due to its high optoelectronics efficiencies relative to indirect band gap group IV, its wide band gap (3.37 eV), high exciton binding energy (E60 MeV) and high dielectric constant, ZnO considered to be an important semiconductor material for variety of applications in the visible and near ultraviolet region[2-3].ZnO nanoparticles have received great attention because of their unique catalytic, electrical, gas sensing, optical properties, their non-toxicity, good electrical, optical, and piezoelectric behavior and other advantages such as their low cost and extensive applications in diverse areas are some of the reasons for this extensive attention.ZnO nanoparticles can be prepared on a large scale at low cost by simple solution based methods, such as chemical precipitation, sol-gel synthesis, and solvothermal/hydrothermal reaction[4-6].

Environmental problems associated with hazardous wastes and toxic water-pollutants have attracted muchattention. Organic dyes are one of the major groups of pollutants in wastewaters released from textile and other industrial processes. Among various Physical and biological techniques for the treatment of pollutants, precipitation, adsorption, air stripping, flocculation, reverse osmosis, and ultra-filtration can be used for color removal from textile effluents[7].One of the main environmental applications of

nanotechnology is inthe water sector. Heterogeneous photocatalysis, one of the advanced oxidation processes (AOPs), is a cost-effective treatment method for the removal of toxic pollutants from industrial waste water sowing to its ability to convert these into safer end products such as CO_2, H_2O, and mineral acids[8-9]. Semiconductor nanoparticles, as heterogeneous photocatalysts, have attracted much interest due to their size tunable physical and chemical properties.Transition metal from bulk to nanosize, displays quantum mechanical properties and increased dominance of surface atoms, which give rise to unique photo-physical and photo-catalytic properties to the nanomaterial. Transition- metal oxides have unique catalytic functions due to rapid generation ofelectron-hole pairs by their photo-excitation and the highly negative reduction potentials of excited electrons[10]. The most effective functional material for photocatalytic applications are nanosized semiconductor oxide.As one of important semiconductor photocatalysts, nanostructure ZnO has attracted more interestsbecause of its considerable photocatalytic efficiency and good stability[11]. ZnO offers low cost, mild reaction condition, high photochemical reactivity, while affording the use of UV light.

In this context ZnO has been synthesized by precipitation method.The nanoparticle has been characterized by TEM, XRD, UV-Visible spectroscopy and FTIR. Also, the degradation and kinetics of photocatalytic degradation of phenol red dye using assynthesized ZnO nanoparticles as photocatalysts have been reported.

Experiments:

Materials:

The chemicals used Zinc acetate, Triethanolamine and sodium carbonatein the preparation were of analytical reagent grade purchased from S-D Fine Chem.Ltd. Phenol Red was obtained from Merck, India and used assuch without any further purification. Double distilled water was used in all the studies to make the solutions of compounds of desired concentration for the irradiation experiments.

Preparation of ZnO Nanoparticle:

The zinc oxide nanoparticles were synthesized by precipitation the surfactant solution containing triethanolamine and zinc acetate with sodium carbonate. Triethanolamine used as a stabilizer and 50ml of 0.1M zinc acetate was stirred for 30 minutes. To that solution 0.1M of sodium carbonate was added. The solution turns milky white in colour after addition of sodium carbonate. After the reaction, the suspension was kept under stirring for 5 hours at room temperature, precipitate was filtered washed with double distilled water and absolute ethanol several times, dried under vacuum for 12 hours. Then zinc oxide nanoparticles were obtained.

$Zn(CH)_3(COO)_2 + Na_2CO_3 = ZnO + CH_3COONa + CO_2$

This product were then used for characterization and also for the degradation of organic pollutant.

Photocatalytic activity test:

The photocatalytic activity of ZnO nanoparticle was studied using Phenol red, a widely used dye. The concentration of ZnO nanoparticle were fixed to be 1g/l. It wasmixed in Phenol red solutions of different concentration of 10, 20, 30, 40 and 50 ppm and absorbance were recorded by using a UV-Visible Spectrophotometer at an wavelength of 650nm (Max. absorbance at 650nm in visible region).The experiment was performed as follows:

Different concentration of dye solution as 10, 20, 30, 40 and 50 ppm were prepared and to each solution fixed amount of ZnO nanoparticle was added. The concentration of the oxide added to be 1g/lit. The λmax for the dye solution was determined and to that wavelength absorbance was noted for the degradation of the dye. The absorbance was recorded after addition of metal oxide. This absorbance is noted to be as A_o. And after UV irradiation, the absorbance was again measured at t intervals of time. The total irradiation time is 60 min. The extent of photocatalytic activity of ZnO in Phenol red can be determined by measuring the absorbance of the solution. The degradation of Phenol red can be evaluated by using the formula:

$$\text{Degradation (\%)} = \frac{Co - Ct}{Co} \times 100 = \frac{Ao - At}{Ao} \times 100$$

whereC_o is the initial concentration, C_t is the concentration at t min. A_0represents the initial absorbance and A_t represents the absorbance after t min reaction of the Phenol red at the characteristic absorption wavelength of 650 nm.

Physiochemical techniques:

The infrared spectrum of the solidZinc oxide nanoparticle was recorded by Shimazdu FT-IR Spectrometer. The nanoparticle was mixed with KBr powder and spectra was measured.The particle size of the synthesised nanoparticles was determined by high resolution transmission electron microscopy (HRTEM) operating on TEM, EDAX Boronusing an accelerating voltage of 200 kV. The obtained nanoparticles were examined by a Brucker D8 advance X-ray Diffractometer with Cu K radiation (λ = 1.54 Å) to check the phase system and purity of the sample.For absorbance spectra and study of photocatalytic activity, Shimazdu 1800 double-beam UV–visible spectrophotometer was used.

Result and Discussion:

XRD pattern for ZnO nanoparticle:

Figure 1.shows the XRD patterns of the synthesized ZnO nanomaterial annealed at 400^{o}C using Cu Kα radiation (λ = 1.5406^{o}A). All the diffraction peaks can be well indexed to the crystalline hexagonal phase of the ZnO nanomaterial, with lattice constants of a=3.264Å, d=5.219Å. The results indicate that the samples consist of pure phase and are crystalline in nature.The XRD peaks of ZnO can be found to (100), (002), (101), (103) and (200)at a diffracting planes at 2θ = 31.37^o, 32.72^o, 35.92^o, 47.22^o and

62.34°respectively indicates the formation of hexagonal phase pure wurtzite structure of ZnO (from JCPDF no 79-0208). The crystalline size of ZnO can be calculated using Scherrar's formula:

$$D = \frac{0.94 X \lambda}{\beta Cos\theta}$$

Where 'λ' The wavelength of X-rays (1.5406 for Cukλ)

θ is the Bragg's angle

β is the full width at half maximum.

The broad peak of XRD patterns clearly indicates that particle size is of nanometer dimension[12]. The lattice constant and other parameters are calculated using relation[13].

$$a = d\sqrt{h^2 + k^2 + l^2}$$

where,

(a) is lattice constant; d is inter planar spacing; (hkl) are Miller Indices.

X-ray density is calculated using relation:

$$dx = \frac{8M}{N_A X a^2}$$

where

M is molecular weight of the composition; N_A is Avagadro's number, (a) is lattice constant.

The average crystalline size is found to be 23 nm.

Table 1: Calculation of parameters of ZnO nanomaterial

Nanomaterial	hkl	2θ (degree)	Interplanar spacing 'd'	X-ray density (x X 10^{-22} g/cm^3)	Crystalline size (nm)
ZnO	100	31.374	2.848	0.1740	28.30
	002	32.72	2.734	0.2604	26.20
	101	35.92	2.497	2.4550	23.60
	102	47.22	1.922	6.0778	18.66
	110	56.28	1.560	4.921	23.34
	200	62.34	1.483	4.1437	15.24

UV-Visible Spectroscopy:

UV– visible absorption of synthesized Zinc oxide solution illustrates a wide absorption peak centered at 380 nm.The absorption band of the ZnO nanoparticles have been shows a red shift due to the decrease in the band gap energy of the particle.The maximum absorption of the nanoparticles shows at 380nm and band gap energy was calculated to be 3.26 eV.

The optical band gap, Eg, of thesamples are determined from the absorbance spectra, from the given equation:

$$E = hc/\lambda$$

$$E = 1240/\lambda$$

Where λ is the maximum wavelength and E is the band gap energy.

FTIR Spectra:

Fig.3 shows the IR spectra for the sample product ZnO nanoparticle. IR spectra shows characteristic absorption peaks at 3317 and 2897 cm^{-1} whichare attributed to the -OH stretching vibrations of water absorbed from the surrounding. The two bands at 1533 and 1392cm^{-1} can be assigned to asymmetric and symmetric vibrations of carboxyl group respectively[14].However, the strong peaks at υ = 453 $cm^{-1}$is attributed to the stretching vibrations if Zn-O bonds[15] and confirms the formation of product.

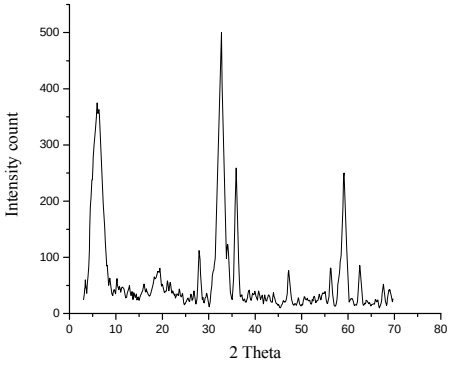

Fig. 1 XRD pattern of ZnO nanoparticle

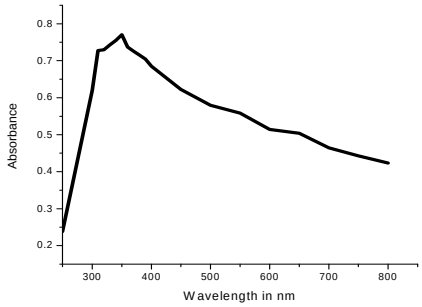

Fig. 2 UV-Vis absorbance spectra for ZnO

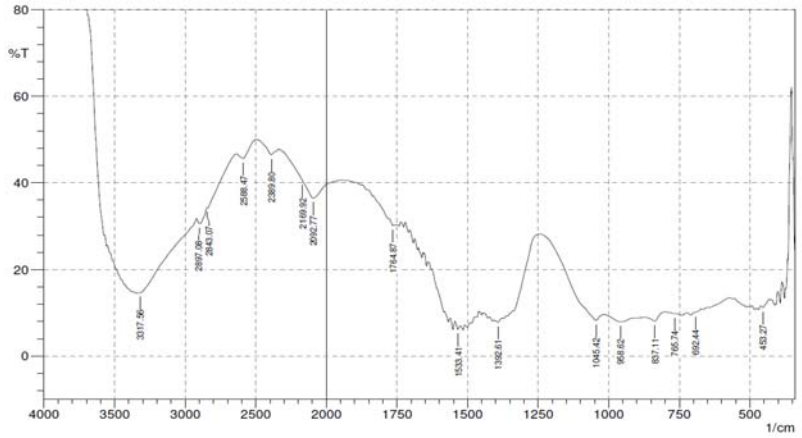

Fig 3. FTIR spectra for ZnO nanoparticle

TEM:

Fig.4a shows the TEM image of synthesized ZnO nanoparticles. The ZnO particles are nearly spherical in shape with more agglomeration. The ZnO prepared by this method are rather well separated with an average size of approximately 20-25 nm which is in good agreement with the grain size calculated by Debye-Scherrer formula.Fig. 4b shows the corresponding diffraction pattern of ZnO nps. The image shows the ring pattern and confirms the peak positions than in the X-rays diffraction pattern arefar less defined than those produced by bulk materials.

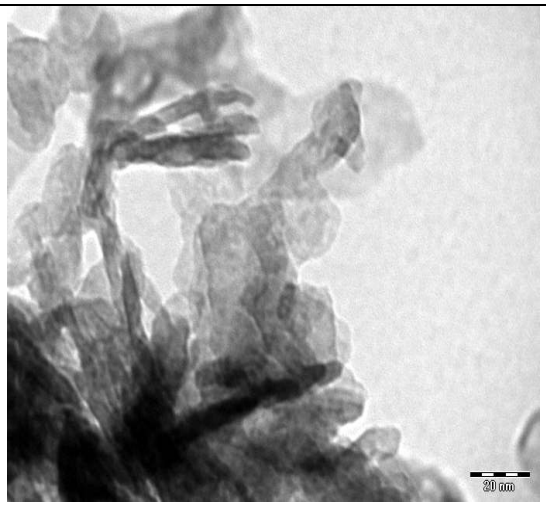

Fig. 4a TEM image of ZnO nps

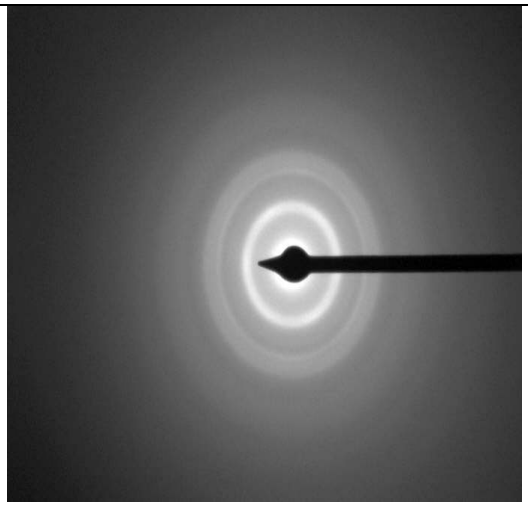

Fig. 4b SAED pattern for ZnO nps

Photocatalytic degradation:

According to the principles of ZnO photocatalysis[16-17], the conduction-band electrons andvalence-band holes are generated on the surfaces of ZnO thin films when they are illuminated by UV light with energy exceeding or equaling to its band gap energy. Holes can react with wateradhering to the surfaces of ZnO thin films to form highly reactive hydroxyl radicals (OH^*). Meanwhile, on the surfaces of the thin films, oxygen is reduced as an electron acceptor to superoxide and this leads to production of hydroxyl radicals (OH^*). The formed radicals have a powerful oxidationability to degrade organic dye.

The highest percent of PR photo degradation is observed for 10ppm solution while the lowest percent of PR photo degradation is observed for 50 ppm as shown in fig 5b. Comparison studies of the dye solution demonstrates that the photocatalytic properties of the ZnO material decreases with increase in higher concentration of pollutant. At lower concentration of the organic pollutant, loading much of light may be transmitted through the solution. However reaction rates is almost same for the different concentration of the dye but the degradation percentage of the pollutant decrease with the increase in pollutant concentration. The photocatalysts ZnO was found to be efficient for the decomposition of the organic pollutant. The decrease in percentage degradation can be explained in terms of complete utilization of

incident photons striking on the catalyst surface or may be possible explanation for this behavior is that as the concentration of the pollutant increases, more and more molecules of the compound get adsorbed on the surface of the catalyst therefore the requirement of the catalyst surface needed for the degradation also increases. Hence the generation of OH^- and O_2^- on the surface of catalyst does not increase; since the amount of catalyst is constant. Hence the degradation efficiency of the nanoparticle decreases with the increase in concentration of the pollutant.

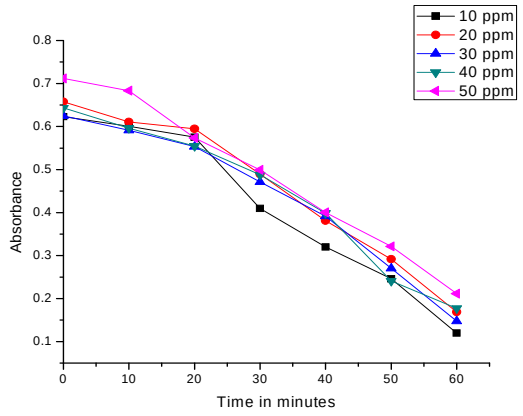

Fig. 5a Depletion in absorbance as a function of time

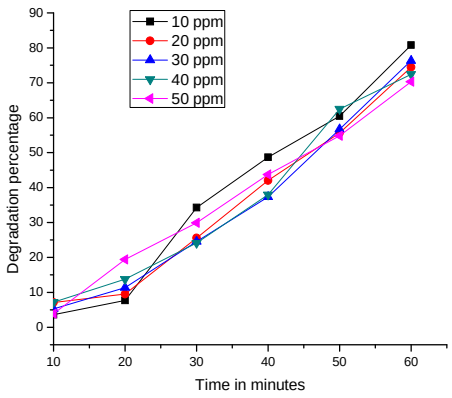

Fig. 5b Plot of percent photocatalytic degradation v/s irradiation time

Table 2: Degradation percentage of Phenol red dye using as-synthesized nanoparticle

Concentration of Methyl red	Time in min	Degradation %	K (min/ l min)
10 ppm	60	81%	5.46×10^{-3}
20 ppm	60	76%	5.41×10^{-3}
30 ppm	60	74%	5.57×10^{-3}
40 ppm	60	72%	5.58×10^{-3}
50 ppm	60	70%	5.58×10^{-3}

Conclusion:

ZnO nanoparticles has been synthesized by precipitation method using very easy, cheap and convenient process. The XRD study has shown the formation of hexagonal crystal structure. FTIR and UV-Visible spectroscopy shows the existence of ZnO nanoparticles. Photocatalytic study revealed that ZnO decomposes Phenyl red dye. The performance of ZnO nanoparticles indicates that it can be used as a photocatalyst for removal of organic contaminants present in water.

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