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Synthesis, Characterization and Photocatalytic Application of Gd Doped ZnO Nanoparticles

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Zinc oxide and gadolinium doped zinc oxide nanoparticles were fabricated using sol-gel method in aqueous media by using sodium dodecyl sulphate as a surfactant. The nanoparticles were characterized by using TGA-DSC, XRD, SEM and TEM. Photocatalytic activity of nanoparticles was studied by photocatalytic degradation of methylene blue, which is an industrial pollutant and highly neurotoxic. The average particle size of nanoparticles calculated by TEM is 22 nm. Photocatalytic degradation of methylene blue was observed under UV-radiation showed first order rate constant (k) is 0.1031, correlation constant (R^2) is 0.9898 and percentage degradation is 26.146 %.

Keywords: Gd/ZnO, Sol-gel method, Photocatalytic degradation.

INTRODUCTION

Preparation of metal oxide nanoparticles with desired morphologies for catalytic process is still an ultimate challenge in material science research[1]. Zinc oxide is a semiconductor nanomaterial with a band gap of 3.3 eV and widely used metal oxide nanomaterial due to its mechanical, electrical, optical, catalytic, biomedical and chemical sensing properties[2]. In order to improve the properties of ZnO, it is usually doped with metallic ions such as rare earth metals or transition metals. Research shows that doping of rare earth metals on ZnO leads to decrease in near band gap due to new unoccupied 4*f* energy state[3]. Doped ions also act as charge trapping sites and reduce electron-hole recombination and show positive result on catalytic properties of nano ZnO[4].

The reuse and recycling of wastewater effluent is going to be a major issue and becoming a necessity for water utilities all above the world. The presence of hazardous organic pollutants in industrial and domestic waste is a big hindrance as regards widespread acceptance of recycling of water[5]. These pollutants directly affect the health of ecosystem and present a threat to human beings by contamination of drinking water supplies.

Heterogeneous photocatalytic oxidation process using catalyst such as TiO_2, ZnO and UV light has demonstrated excellent results by degrading persistent organic pollutants and converting them to more biologically degradable and less toxic substances[6]. TiO_2 is universally considered as most active photocatalyst but ZnO has advantage over TiO_2 due to low cost and it absorbs over a large fraction of UV spectrum as both have almost similar band gap energy[7].

Zinc oxide nanoparticles can be fabricated by different methods such as, micro emulsion technique[8], sol-gel method[9], spray pyrolysis method[10], hydrothermal method[11], laser ablation[12] and levitation gas condensation process[13].

In present study ZnO nanoparticles and Gd doped ZnO nanoparticles are synthesized by simple and cost effective sol-gel method both in aqueous media and using surfactant. Surfactants play an important role in synthesis of metal oxide nanoparticles because of their effect on particle growth, flocculation and coagulation. It is reported that anionic surfactant like SDS gives better results than cationic surfactants[14]. The effect of ZnO and Gd doped ZnO was investigated by photodegardation of methylene blue. Prepared samples were characterized by means of TGA/DSC, FTIR, UV/Vis, XRD, SEM and TEM.

EXPERIMENTAL

Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), sodium hydroxide and oxalic acid were purchased from Merck, gadolinium chloride hexahydrate, sodium dodecyl sulphate and methylene blue was purchased from Sigma Aldrich. All chemicals were used without further purification. The characterization was done by using thermogravimetric analysis-diffraction scanning calorimeter (TGA-DSC, Q600 TGA DSC), Fourier transform infrared (FTIR) spectroscopy (Bruker Alpha Platinum ATR), X-ray diffractometer analysis (X'pert PRO, PANAnalytical), scanning electron microscope (SEM-Hitachi S-3400) and transmission electron microscope (Phillip CM12 microscope).

General procedure

Synthesis of ZnO nanoparticles: Synthesis of zinc oxide nanoparticles was done by mixing 0.01 M (96.2 mg/50 mL DW) zinc acetate dihydrate and 0.02 M of NaOH solution and continuous stirring for 2 h at 80 °C to get precipitates. The pH of solution was maintained at 4.5 by using 0.01 M oxalic acid. Precipitates were centrifuged and then dried in oven at 100 °C for 2 h. Dried Precipitates were calcined at 450 °C for 2 h[15]. The same procedure was repeated for synthesis of ZnO in presence of surfactant, 0.008 M SDS was used after adding precursors.

Synthesis of Gd doped ZnO nanoparticles: Synthesis of gadolinium doped zinc oxide nanoparticles was done by adding 50 mg of ZnO nanoparticles in 10 mL of gadolinium chloride hexahydrate solution and was heated at 80 °C for 1 h with continuous stirring, pH was maintained by using 0.01 M oxalic acid solution. The same procedure was used for ZnO which was synthesized in presence of surfactant.

Photocatalytic activity: Photocatalytic activity of zinc oxide and gadolinium doped zinc oxide was analyzed by measuring the photocatalytic degradation of methylene blue dye. 50 mL of 10 ppm solution of dye was taken in a beaker and 10 mg catalyst was added in it, the aqueous solution of dye was stirred continuously in dark for 30 min to establish adsorption/desorption equilibrium and then placed in UV-light. On the basis of Beer-Lambert law calibration was done at wavelength of maximum absorptivity, λ_{max} 665 nm. 5 mL of sample was drawn after 30, 60 and 120 min exposure of UV-light and absorbance of methylene blue was determined by means of UV-visible spectrophotometer at 665 nm in kinetics mode for 60 min. The decrease in absorbance was observed by UV-visible spectrophotometer due to catalytic degradation of ZnO and Gd/ZnO. Graphs were plotted between $\ln(A-A_\infty)$ *vs.* time using a first-order rate equation $\ln(A-A_\infty) = -kt + \ln[A_o]$[16]. The value of rate constants k was calculated from the slope of the graphs (Fig. 1).

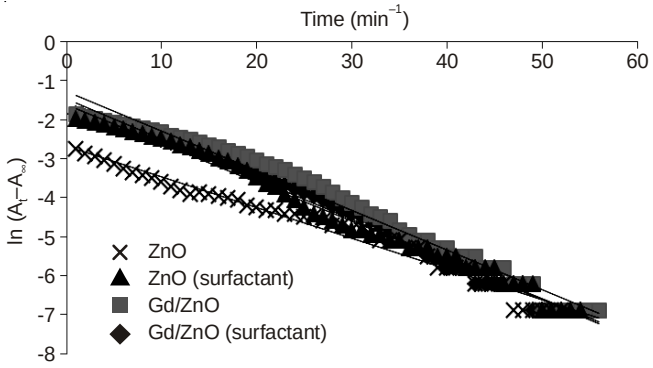

Fig. 1. First order plot between ln (A_t-A_∞) *vs.* time (min^{-1})

RESULTS AND DISCUSSION

Zinc oxide and gadolinium doped zinc oxide nanoparticles were analyzed by FTIR. The peak obtained at 3419 and 3418 cm^{-1} was due to stretching vibration of -OH. The peaks obtained at 2358 and 1043 cm^{-1} are due to C-O, which indicates the adsorption atmospheric CO_2[17] on highly reactive surface area of nanoparticles. The main peak of Zn-O[18] is present at 1551 cm^{-1} as shown in Fig. 2(a) and 1551, 1540 cm^{-1} as shown in Fig. 2 (b). The presence of Gd[19] in doped sample is confirmed by peak at 1396 and 669 cm^{-1} as shown in Fig. 2(b).

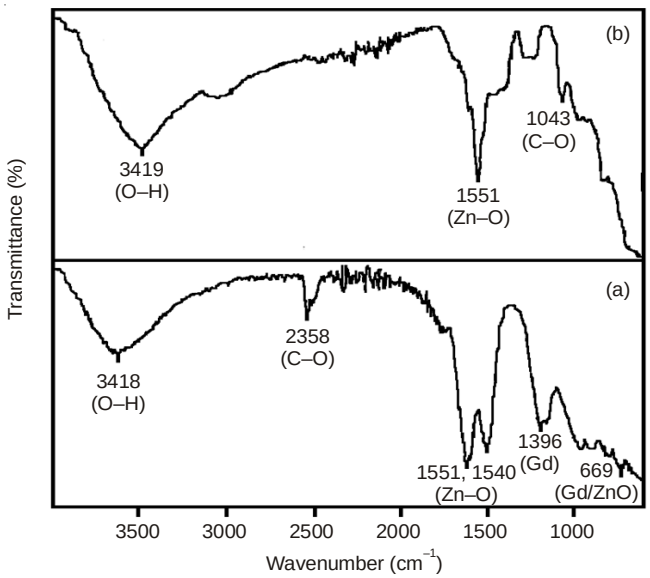

Fig. 2. FTIR spectra (a) ZnO (b) Gd/ZnO

Thermogravimetric analysis was performed at the temperature range 0 to 800 °C. TGA curve of uncalcined samples represent major mass loss in two steps. In the first step from temperature range 75-160 °C weight loss is due to removal of surface adsorbed water. This is shown from the figure. In second step mass loss takes place at temperature range 360-420 °C, there is very sharp curve at this temperature range which represents major weight loss due to formation of metal oxide from hydroxide[17] (shown in Fig. 3(a) and (b)). In first step mass loss is from 98.5-70 % and in second step mass loss is up to 39 %. DSC curve shows formation of ZnO and Gd doped ZnO in two endothermic reactions at 160 and 390 °C.

X-Ray diffraction technique is used to identify the crystallite phase and particle size of ZnO and Gd doped ZnO nanoparticles (Fig. 4). Broadening of peak represents the nanometer size of the crystallite; average particle size can be calculated by Scherer equation[20,21]:

$$D = 0.89 \cdot \lambda / \beta \cdot \cos\theta$$

where D is average crystallite size, λ is wavelength used for measurement which is 1.5406 Å, β is full width at half maximum (FWHM) of the XRD all peaks, K is Scherer's constant and θ is the Bragg diffraction angle. Particle size is given in Table-1.

TABLE-1
DIFFERENT PARAMETERS AND GRAIN SIZE OF CRYSTALLOGRAPHIC PLANE (101) OF NANOPARTICLES

Catalyst	Medium used	Crystallite size (nm)	2θ (°)	FWMH	d-spacing (Å)
Gd/ZnO	Surfactant	2.58	31.961	0.5510	2.800
Gd/ZnO	Aqueous	2.61	36.212	0.5510	2.475
ZnO	Surfactant	4.55	36.300	0.3149	2.474
ZnO	Aqueous	4.58	36.011	0.3198	2.494

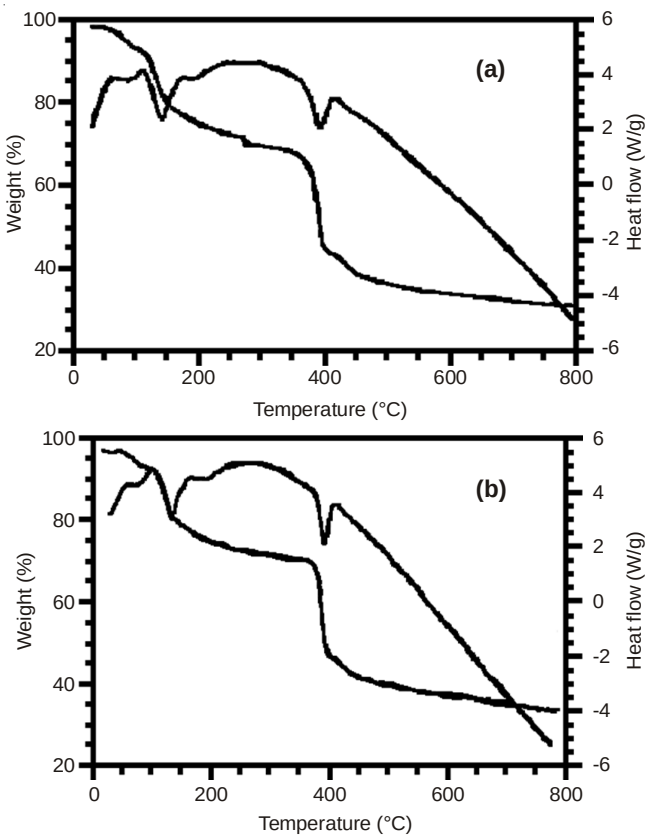

Fig. 3. TGA graph of Gd/ZnO (a) without surfactant (b) with surfactant

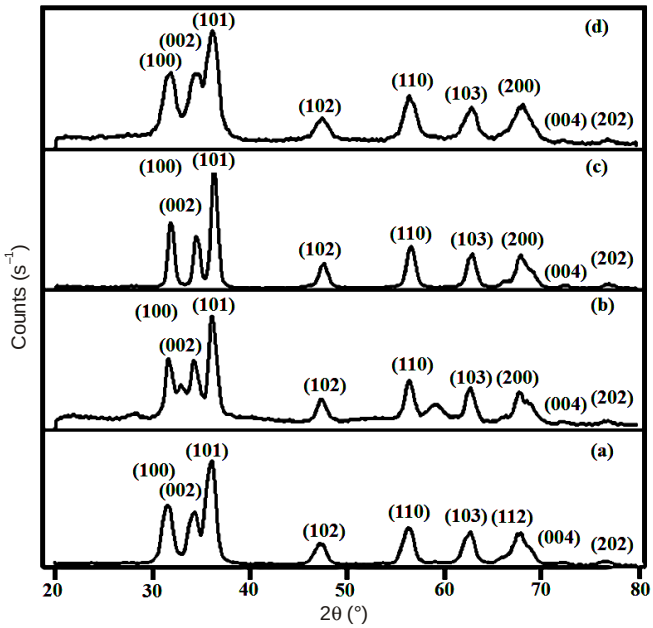

Fig. 4. XRD pattern (a) ZnO nanoparticles without surfactant (b) ZnO nanoparticles with surfactant (c) Gd/ZnO nanoparticles without surfactant (d) Gd/ZnO nanoparticles with surfactant

Morphology of nanoparticles was determined by using scanning electron microscopy (SEM). Fig. 5 shows more or less spherical particles but particles show a high degree of agglomeration. This is most probably due to the presence of NaOH in reaction mixture which cause sudden raise of temperature and finally cause agglomeration. Doping of Gd is also visible in Fig. 5.

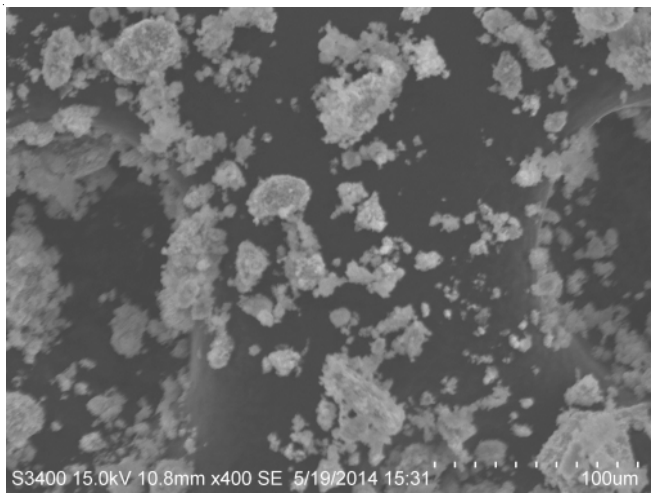

Fig. 5. SEM image of Gd/ZnO nanoparticles

Transmission electron microscopy (TEM) analysis was performed to determined particle size and morphology of nanoparticles. Fig. 6 shows the TEM image of Gd doped ZnO nanoparticles TEM image confirms the formation of Gd doped ZnO nanoparticles after annealing the sample for 2 h at 450 °C and average particle size was 22 nm. TEM image shows spherical shape and agglomerations of nanoparticles.

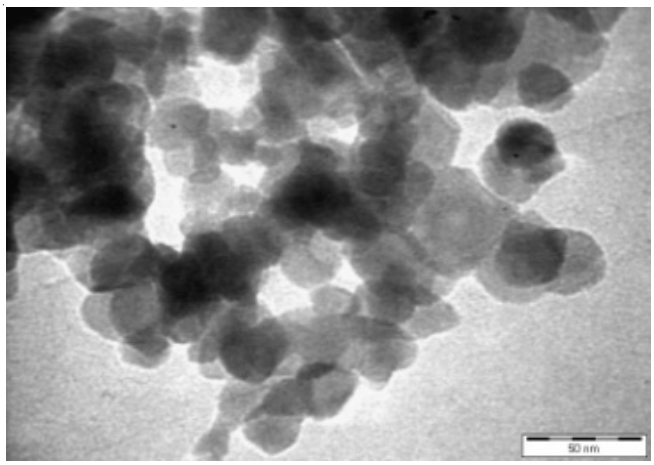

Fig. 6. TEM image of Gd/ZnO nanoparticles

Catalytic activity of ZnO and Gd doped ZnO: Photocatalytic activity is measured by rate of photocatalytic degradation of methylene blue under different conditions at different time intervals. Methylene blue is an organic dye and gives λ_{max} at 665 nm. To determine catalytic activity, 50 mL of 10 ppm methylene blue solution was stirred for different time values in the presence of ZnO and Gd doped ZnO nanoparticles as catalyst. It was observed Gd doped ZnO nanoparticles synthesized using surfactant show maximum degradation under UV light for 2 h. Fig. 7 indicates that catalyst fabricated by using surfactant displays more degradation of Methylene blue as compared to that catalyst which synthesized in aqueous media. Similarly Gd doped ZnO nanoparticles degrade dye more efficiently than undoped catalyst samples.

Nanoparticles synthesized in presence of surfactant shows enhanced catalytic activity because of less coagulations and small particle size as compared to nanoparticles synthesized

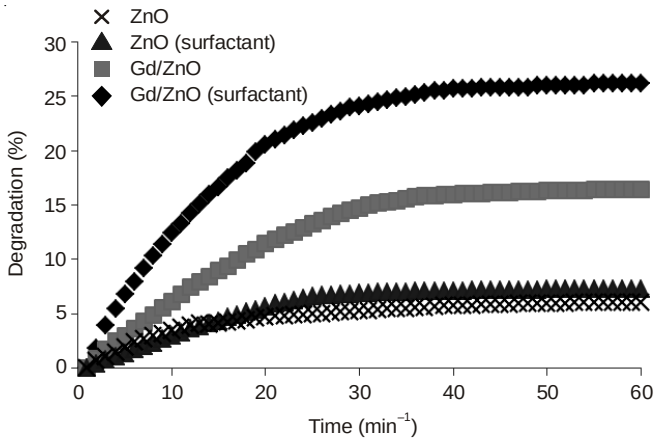

Fig. 7. Percentage degradation of methylene blue by catalyst, X ZnO, ZnO (surfactant), Gd/ZnO and Gd/ZnO (surfactant)

without surfactant (Table-2) showing that on increasing percentage degradation of dye k-value also increases. Small particle size increase surface area of nanoparticle results in increase in catalytic activity. Gadolinium doped nanoparticles also increase the catalytic activity because band gap energy of pure ZnO is 3.3 eV, the band gap energy of Gd doped ZnO samples[3] is smaller than 3.3 eV which is in agreement with the fact that doped ions will introduce new electronic levels inside the ZnO band gap results in higher catalytic activity of Gd doped ZnO catalyst. Order of catalytic efficiency of nanoparticles is:

$$Gd/ZnO_{(surfactant)} > Gd/ZnO > ZnO_{(surfactant)} > ZnO$$

TABLE-2
PERCENTAGE DEGRADATION AND k-VALUES OF PHOTOCATALYTIC ACTIVITY

S. No.	Catalyst	Medium used	Degradation (%)	k-value
1	Gd/ZnO	Surfactant	26.146	0.1031
2	Gd/ZnO	Aqueous	16.470	0.1015
3	ZnO	Surfactant	7.320	0.0994
4	ZnO	Aqueous	6.075	0.0787

Conclusion

Gadolinium doped ZnO nanoparticles were prepared by sol-gel method in aqueous media and using SDS as surfactant below its CMC value. Prepared samples were chracterized by TEM, SEM, XRD, TGA and FTIR. XRD, TEM and SEM confirmed the nanostructure for the prepared samples. Gadolinium doped ZnO nanoparticles were found effective catalyst for the degradation of methylene blue. Highest percentage degradation was obtained with Gd doped ZnO nanoparticles fabricated in the prescence of surfactant. Percentage degardation and k-value is directly proportional to each other. By increasing percentage degradation k-value is also incresed. Results are showing that by increasing percentage degradation from 6.075 to 26.146 the k-value also increased from 0.0787 to 0.1031 min^{-1}.

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