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Synthesis and Characterization and Photocatalytic Studies of La, Ce co-doped ZnO Nanoparticles

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Abstract—*In this study, pure and lanthanum and cerium co doped ZnO ($Zn_1La_0Ce_0O$, Zn0.98La0.01Ce0.01O, Zn0.96La0.02Ce0.02O) ZnO nano particles have been successfully synthesized by co precipitation method using the mixture of Zinc acetate, Lanthanium acetate and Cerium acetate in distilled water . The powders were calcination at 400°C for1h. The effect of lanthanum and Cerium incorporation on the structure and morphology was examined by X-ray diffraction (XRD), Scanning Electron Microscope (SEM),) The photocatalytic activity of rare earth La Ce co- doped ZnO nanoparticles was studied by performing the degradation of Rhodamine B dye solution under UV light irradiation within 0–40 mins. The Rhodamine B dyesolution was considerably photodegraded by Zn0.98La0.02-Ce0.02O photocatalyst under UV light irradiation within 35min.The average particlesize of the synthesized pure and co doped ZnO nanoparticles is calculated using the Scherrer formula and is found to be of less than 50 nm.*

1. INTRODUCTION

Semiconductor nanoparticles are widely used as photocatalysts for converting light energy into useful chemical energy, which can be harnessed in wide range of applications. For example, semiconductors like TiO_2 and ZnO act as sensitizers for light induced redox processes because their electronic structure which comprises of afilled valence band and an empty conduction band [1].When the energy of a photon striking the material is in excess of band gap energy of that semiconducting, an electron is promoted from the valance band into the conduction band leaving behind a hole. The electrons and holes in the valance band and conduction band formed in this way can recombine and dissipate the incoming energy as heat, and get trapped in metastable surface states. [2]. If the recombination can be prevented with suitable surface defect of scavenger state acting as trap for electrons and holes then redox reactions may occur due to the remaining free electrons and holes. The holes in valence band act as powerful oxidants, while the electrons in conduction band act as reductants [3, 4]. Majority of the organic photodegradation reactions occur due to the high oxidizing power of the holes either directly or indirectly.

Industrial pollutants in air water are a potential threat to human health.. Therefore enormous efforts are being put in to remove hazardous chemicals, especially organic pollutants from waste water. The photocatalytic reaction is a low cost and environmental friendly alternative treatment method to convert the organic compound into simpler and harmless compounds for tackling environmental pollution as per the reported literature [1].Zinc Oxide is transparent and exhibits electro conductive and piezo electric properties . Zinc Oxide is an excellent antibacterial agent and shows remarkable absorption for uv light. ZnO has direct band gap energy of 3.37eV and large excitation binding energy of 60 meV at room temperature making it the most exciting semi conductor as these properties provide excitonic emission more efficiently even at high temperature. ZnO is particularly promising because of their exceptional optical/electronic properties and attractive possible applications in various fields such as efficient solar cells [5], energy saving light emitting diodes [6], emission, gas sensors [7], fluorescent materials and solar cells [8**].**

Rare earth doping enhances the properties of ZnO. The phenomenon of quantum confinement leads to exotic physio-chemical properties.

Optical properties are further enhanced in doped luminescent nanoparticles.. ZnO nanoparticles at different Lanthanum (La) and Cerium (Ce) doping concentration have been prepared via co precipitation route. Characterization of the sample has been done by XRD, SEM, and FTIR analysis.

2. EXPERIMENTAL

2.1 Materials and methods:

Pure ZnO nano particles *ZnO (*$Zn_1La_0Ce_0O$ were synthesized by taking Zinc-Acetate-2-Hydrate [$Zn(O_2CCH_3)_2$. 2(H_2O)] in distilled water and stirring for 1 hour. Triethyamine was slowly added to control the morphology and size..LaCe co-doped ZnO nanoparticles (Zn0.98La0.01Ce0.01O, Zn0.96La0.02Ce0.02O) were prepared by using co-precipitation method. Mole fraction of the constituent elements in the nanoparticles was controlled by adjusting the La, Ce to Zn weight ratio. The high purity chemicals (Sigma Aldrich, purity 99 % purity) such as Zinc-Acetate-2-Hydrate [Zn(O2CCH3)2. 2(H2O)], Lanthanum (III) Acetate

Hydrate[La(CH3COO)3.1.5H2O)] and Cerium (III) AcetateHydrate-4-Hydrate [Ce(CH3COO)3.4H2O)] (Loba Chemie)were used as starting material and also dopant sources, respectively. Distilled water and Triethylamine (Analytical Grade) were used as solvent and stabilizer, respectively. The above chemicals were used without any further purification. An appropriate amount of Zinc Acetate and was dissolved in distilled water and stirred at 60 _C for 1 h. Then, Lanthanum (III) Acetate Hydrate and Cerium (III) Acetate Hydrate-4-Hydrate with mole fraction (0.01and0.02) was added to it and triethylamine was slowly added for size and morphological control, the final solution was stirred for additional 1 h. Three samples were prepared with mole fraction varying from 0.00 to 0.02. The clear and homogeneous solutions were evaporated on a hot plate The resulting nanoparticles were washed with ethanol to remove the impurities present if an. and further isolated by centrifugation . The nano particles were subsequently, t annealed at 400 C in muffle furnace atmosphere for 1h followed by furnace cooling. Standard conditions for synthesizing the LaCe co-doped ZnO nanoparticles are shown in Table 1.

Table 1: Standard conditions for synthesis La, Ce Co doped nanoparticles

Mole Fraction (La and Ce)	Zinc Acetate	Lanthanium Acetate	Cerium Acetate	Triethylamine
0.00	0.5	0.000	0.000	0.5
0.01	0.5	0.005	0.005	0.5
0.02	0.5	0.010	0.010	0.5

2.2 Characterization

XRD **(XPERTPro, PANalytical JDX-8030, JEOL)** measurements were made using CuK$_\alpha$ radiation to determine the phase and size the samples. The samples were scanned with a scan rate of 0.02^o/s in the scan range of 15 to 60^o. An average grain size calculation of the samples was done by using its XRD peak broadening according to Scherrer formula [9] as given below in Eq. (1).

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

D is the average size of crystallite, B is the broadening of the diffraction line measured at half maximum intensity, λ is the wavelength of the X-ray radiation (1.54052 Å, CuKα) and θ is the Bragg's angle. The instrumental broadening has been considered for the calculation of grain size, and the value of 0.1 is subtracted (calculated using standard silicon sample) from the full-width half maximum (FWHM) value (B value).

The surface morphology of pure and La,Ce was determined by SEM.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction (XRD)-Structural studies

Fig. 1 shows the XRD pattern of pure and La,Ce co-doped ZnO (0.1 and 0.2 mol%) calcined at 400 °C. The strong intensities of diffraction peaks (010), (002), (011), (012), (110),(013), (020), (112), (021), (004), (022) can be indexed to hexagonal structure of ZnO.(JCPDS# 98-002-6593).

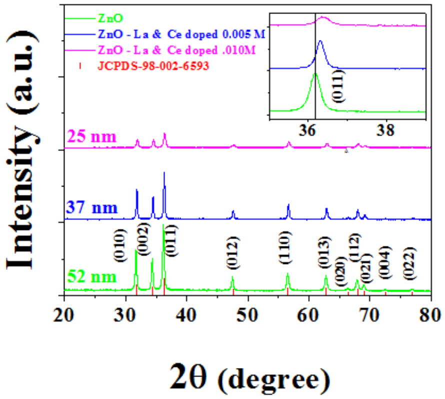


Fig. 1: XRD pattern of pure and La, Ce co -doped ZnO nanoparticles

The particle size of pure and La, Ce co doped ZnO was found. It is observed that as the concentration of dopants increases, the intensity of the peaks decreases which in turn indicates the decreases in size of the nanoparticles.

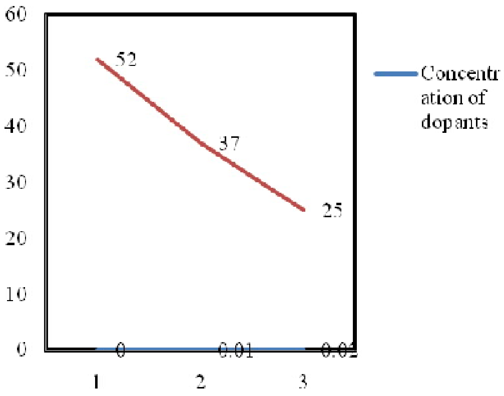


Fig. 2: The effect of Dopant concentration on the crystallite size.

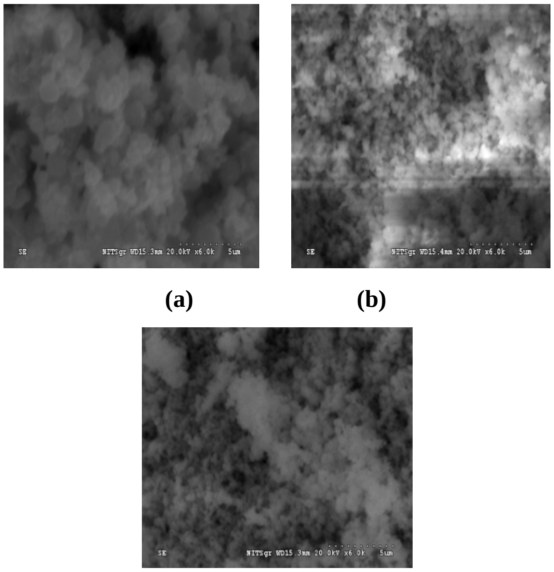
Table 2: Dopant Concentration and Crystallite of La, Ce co doped ZnO nanoparticles

Mole Fraction (x)	2θ	Crystallite size (nm)	Crystal structure
0	36.25	52	hexagonal
0.01	36.43	37	
0.02	36.55	25	

When lanthanum and cerium were doped into ZnO matrix, diffraction peaks of the doped samples are almos tsimilar to those of undoped hexagonal ZnO crystal. Their unchanged crystalline structure indicates that La^{3+} and Ce^{3+} uniformly disperse across the hexagonal ZnO matrix[10].The sharp diffraction peaksindicate that both pure ZnO and La , Ce co-doped ZnO nanostructures have crystalline nature. The large ionic radii of La^{3+} (1.06 A) and Ce^{3+}(1.15 A °) in comparison to that of Zn^{2+} (0.72A°), make substitution difficult, thus distorting the ZnO lattice[11]. Also,compared to un-doped ZnO nanoparticles, increased La and Ce ions doping concentration causes a shift in diffraction peak position of the La Ce codoped ZnO nanoparticles. Hence the expansion of ZnO lattice along the c –axis can be attributed tothe lattice mismatch between La^{3+}, Ce^{3+} and ZnO lattice.

3.2 Microstructural and Compositional studies

The morphological studies were investigated using Hitachi scanning electron microscopy and images are displayed in Fig.3 for pure and La and Ce co doped ZnO nano particles. These images exhibit the formation of nanoparticles of doped ZnO. Crystal formation in solution can be divided into two stages: crystal nucleation and crystal growth. These two stages are responsible for the formation of the ZnO particles with different morphologies.



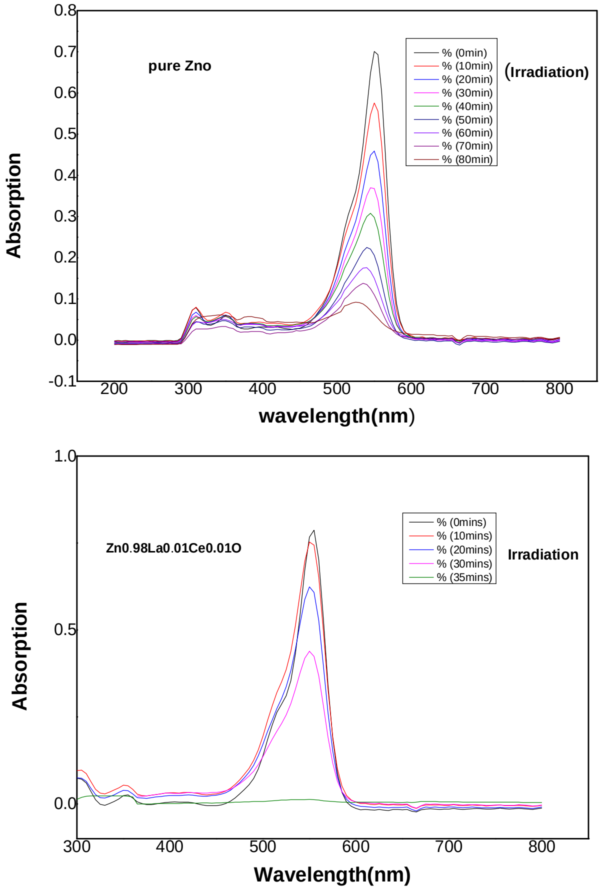
(a) (b)

(c)

Fig. 3: SEM photomicrograph: a) pure ZnO nanoparticles, b) 0.01M La, Ce co doped ZnO c) 0.02M La, Ce co-doped ZnO

3.3 Photocatalytic Activities:

The photocatalytic degradation of doped and un-doped ZnO nanoparticles was investigated in glass beaker under the UV light. The solution for photodegradation measurement was prepared by adding 0.04 g ZnO (undoped) of $Zn_{0.98}La_{0.01}Ce_{0.01}O$, $Zn_{0.96}La_{0.02}Ce_{0.02}O$ nanoparticles and10 mL (20ppm concentration) of Rhodamine B dye in 30 mL of water. Before illumination, the suspension was magnetically stirred in the dark for half an hour for dispersion of catalyst and establishment of adsorption/desorption equilibrium. After that, the suspension was irradiated withUV light. Stirring was continued during the irradiation to keep the mixture in suspension. At given time intervals of irradiation, 3 mL of the dye solution was sampled at given time intervals and centrifugated immediately to remove the nanoparticles. The change in Rhodamine B concentration in each photodegraded solution.was monitored by an ultraviolet–visible (UV–Vis)spectrometer (T80 Uv Vis spectrometer). The degradation of Rhodamine B dye under UV-irradiation at different reaction times (0–40 mins) is shown in Fig. 4a–c. Degradation of dye solution is indicated by decrease in absorbance intensity of with the increase of exposed time. It is clear from the absorbance spectra from Fig. 4a–c that when La Ce codoped ZnO nanoparticles- are used as a photocatalyst, an impressive decrease in concentration of Rhodamine dye solution takes place. On the other hand, when un-doped ZnO particles (Fig. 4a)are used as a photocatalyst, a less decrease in concentration of dye solution takes place. The degradation of dye was fastest with $Zn_{0.98}La_{0.01}Ce_{0.01}O$ as can be clearly seen in picture (figure 4 d).



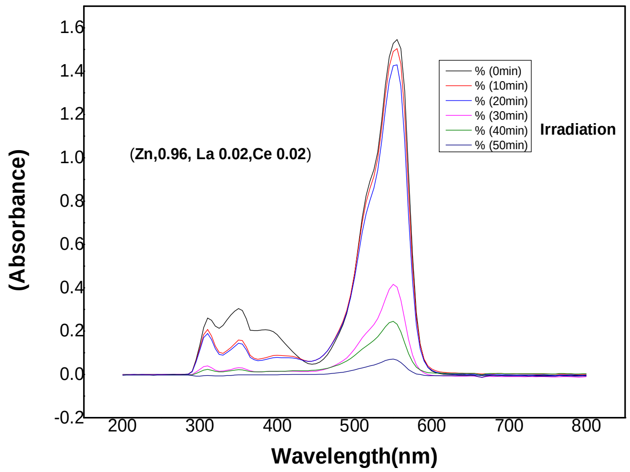


Fig. 4 a–c UV–Vis absorbance Spectral changes of Rhodamine B dye solution during the photocatalytic degradation by un-doped ZnO and La Ce co-doped ZnO nanoparticles under UV irradiation at different times, un-doped ZnO, b Zn0.98La0.01Ce0.01O, c Zn0.96La0.02Dy0.02O,

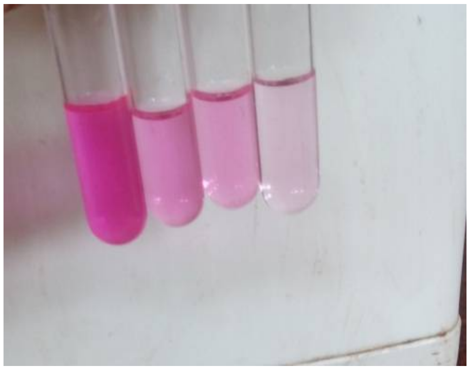


Figure 4 d Photograph of degradation of Rhodamine B dye with $Zn_{0.98}La_{0.01}Ce_{0.01}O$ as catalyst

4. CONCLUSION

Pure and La, Ce co doped ZnO nanoparticles were successfully synthesized by co precipitation method. The XRD pattern of La, Ce co doped ZnO clearly shows the sharp peak obtained from ZnO planes. The particle size of pure and La, Ce co doped ZnO nanoparticles and the has been determined.

The particles crystallized in Hexagonal structure. The morphology of the ZnO particles was obtained from SEM. The investigation of the photocatalytic activity showed that all the La Ce co- doped ZnO nanoparticles exhibit excellent photocatalytic degradation activityof Rhodamine B dye solution as visible light irradiation. $Zn_{0.98}La_{0.01}Ce_{0.01}O$ nanoparticles showed the highest photocatalytic activity of all the La Ce co-doped ZnO nanoparticles and undopedZnO particles.

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