Photocatalytic and Photoluminescence Studies of La, Ce, and Dy Co-doped ZnO Nanoflowers

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Received: 26 April 2021 / Accepted: 26 October 2021 / Published online: 4 January 2022
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Abstract In the present work, ZnO nanoparticles were doped with varying concentration of lanthanum (La), cerium (Ce), and dysprosium (Dy) using a simple and cost-effective co-precipitation approach at low temperatures. The resulting powders were calcined at 500 °C for 1 h using a muffle furnace, to produce La, Ce, and Dy-co-doped ZnO nanoparticles with varying stoichiometry, viz. (Zn0.97La0.01Ce0.01Dy0.01O, Zn0.94La0.02Ce0.02Dy0.02O, Zn0.91La0.03Ce0.03Dy0.03O, Zn0.88La0.04Ce0.04Dy0.04O, and Zn0.85La0.05Ce0.05Dy0.05O). This is a simple approach for doping and does not require a complex equipment, harmful chemical, or sophisticated machinery. The synthesized powders were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) for studying the structure, purity, and grain morphology. Compositional study was done using EDS (SEM/EDS Hitachi 3600 N). The average crystallite size was calculated using XRD and was found to be 35 nm, and it also indicated a hexagonal wurtzite structure with no secondary peaks. A change in morphology from nanorods to nanoflowers was observed as the concentration of dopants increased. Photoluminescence (PL) spectra indicated a redshift in the absorption edge toward the visible region of solar spectrum and this was further confirmed by diffuse reflectance spectra (DRS). The photocatalytic properties of undoped and La, Ce, and Dy-co-doped ZnO nanoparticles were observed by examining the photodegradation of Rhodamine B dye under UV irradiation. The elimination of dye color indicated the total degradation of organic molecule. The results revealed that ZnO photocatalyst with La, Ce, and Dy co-dopant concentration Zn0.85La0.05Ce0.05Dy0.05O exhibited the best photocatalytic performance (95%) as compared to undoped ZnO. The improved photocatalytic performance can be attributed to the increased surface oxygen vacancies and adsorption capacity. The delay in recombination of charge carriers due to creation trap states in the bandgap of ZnO further improves the photocatalytic performance of doped samples.

Keywords La, Ce, and Dy co-doping · Co-precipitation · Photoluminescence · Photocatalyst · Rhodamine B · Rare earths

Introduction

In present times, the advancement in electronics and technology can be credited to improvement in semiconductor nanomaterials. Among the semiconductor nanomaterials, TiO2, ZnS, ZnSe, ZnO, CdSe, indium tin oxide (ITO), etc., exhibit excellent optical properties [1]. ZnO, being a class II-VI semiconductor, has a wide bandgap (3.37 eV), high binding energy at room temperature, better chemical stability, and very high melting point (1975 °C). Owing to its unique properties, ZnO is the most commonly used semiconductor in optoelectronic applications, viz. photocatalysis, photoluminescence, solar cells, field emission displays, etc. Widescale use of ZnO can be further attributed to its low cost, simple synthesis, little toxicity, electron transport capability, and low crystallization temperature [2–7].

Doping, i.e., incorporation of small quantity of impurity ions into the host lattice, can tune and modify the...
properties of semiconductors to suit particular applications [8–12]. Optoelectronic and magnetic properties of ZnO can be easily modulated by doping. Among the materials used for doping, rare earth ions with 4f configuration have gained maximum attention due to their unique luminescence and recombination sites for the electron–hole pairs [13].

Semiconductors used as photocatalysts such as ZnO are crucial in easing the global concerns regarding waste water treatment. Water pollution and the scarcity of water induced by it are the major concerns of the scientific world today. Textile industry and dye production/utilization units are the major contributors toward the water pollution. Large amounts of effluent water containing intense colored toxic dyes are produced by these every day. Rhodamine B dye owing to its high stability and low cost is the most toxic dyes are produced by these every day. Rhodamine B dye is discussed in the present work.

Photocatalysis has evolved as an efficient, cost-effective, and environment-friendly method for wastewater treatment. Semiconductor nanomaterials like TiO$_2$, ZnS, and ZnO are suitable candidates for photocatalysis; however, ZnO is the most commonly used owing to its low cost, inertness to chemicals, non-toxicity, and resistance against corrosion [15–19]. In practical applications, however, ZnO has narrow range of spectral response, and it especially shows response under UV irradiation (\(\lambda < 380 \text{ nm}\)) which contributes to only 6–8% of solar energy whereas visible light contributes 46%. Further, due to less separation between the photo-generated charge carriers, recombination and dissipation of energy takes place in nanoseconds, making it difficult to utilize the photo-generated electrons and holes. These electrons and holes act as powerful oxidizing and reducing agents, respectively, and a delayed recombination can make them suitable for redox reactions, which leads to better photocatalysis [20, 21]. Hence, to obtain a better photocatalyst out of ZnO, its absorption edge needs to be shifted toward the visible region and photogenerated electrons and holes need to have a better charge separation. These requirements can be achieved by doping rare earth ions into the ZnO matrix [22–26]. Monovalent doping of lanthanides, viz. lanthanum (La), cerium (Ce), and dysprosium (Dy) has been extensively studied [27–31]. Among these monovalent rare earth dopants, cerium is distinctly interesting due to its large ionic radius, which causes a localized charge perturbation when substituted into the lattice of ZnO and hence leads to better photocatalysis [32–36]. Few precursors of divalent dopings are available in the literature, showing such doping leads to much better and improved photocatalysis and bandgap tailoring [21, 37–42]. There are no studies on trivalent doping of ZnO in literature. This motivated us to do a detailed analysis of lanthanum, cerium, and dysprosium co-doping into ZnO matrix, and we observed much improved optical properties. The improvement was observed on multiple fronts. We hereby report a facile and cost effective synthesis of La, Ce, and Dy-co-doped ZnO nanoparticles with improved and optimized photocatalytic activities, a better dopant-dependent bandgap, red shift in the absorption edge and much improved charge separation between the photogenerated charge carriers. A better charge separation is a consequence of dopant-induced trap levels in the bandgap of ZnO.

Several methods have been utilized so far for the synthesis of rare earth-doped ZnO nanoparticles which include forced hydrolysis [43], pulsed laser deposition [44], and combustion methods [45]. All these methods are quite complex and require costly machinery, high temperatures, and toxic chemicals.

In the present work, it has been reported a facile, cost-effective, and environment-friendly co-precipitation technique for synthesizing La, Ce, and Dy-co-doped ZnO nanoparticles with varying stoichiometry, viz. Zn$_{0.97}$La$_{0.01}$Ce$_{0.02}$Dy$_{0.01}$O, Zn$_{0.94}$La$_{0.02}$Ce$_{0.02}$Dy$_{0.02}$O, Zn$_{0.93}$La$_{0.03}$Ce$_{0.03}$Dy$_{0.03}$O, Zn$_{0.88}$La$_{0.04}$Ce$_{0.04}$Dy$_{0.04}$O, and Zn$_{0.85}$La$_{0.04}$Ce$_{0.05}$Dy$_{0.05}$O. Optical properties of all dopant concentrations were compared. Structural, morphological, photoluminescence, and bandgap studies were done using XRD, SEM, PL, and DRS, respectively. Composition was authenticated using EDS (SEM/EDS Hitachi 3600 N). Photocatalytic properties of undoped La, Ce, and Dy-doped ZnO nanoparticles were analyzed by observing the decomposition of Rhodamine B under UV light irradiation. The degradation of harmful dye and ensuing removal of color was much improved in La, Ce, and Dy-co-doped samples as compared to the undoped ZnO. The detailed mechanism of photocatalytic degradation of Rhodamine B dye is discussed in the present work.

**Experimental Procedure**

A low cost, facile and environment friendly co-precipitation approach was used for synthesizing La, Ce, and Dy-co-doped ZnO nanoparticles (Zn$_{0.97}$La$_{0.01}$Ce$_{0.01}$Dy$_{0.01}$O, Zn$_{0.94}$La$_{0.02}$Ce$_{0.02}$Dy$_{0.02}$O, Zn$_{0.93}$La$_{0.03}$Ce$_{0.03}$Dy$_{0.03}$O, Zn$_{0.88}$La$_{0.04}$Ce$_{0.04}$Dy$_{0.04}$O, and Zn$_{0.85}$La$_{0.04}$Ce$_{0.05}$Dy$_{0.05}$O). The mole fraction of the constituent ions was maintained by controlling the weight ratio of dopants La, Ce, and Dy to host Zn. The starting material and the dopant sources used, viz. zinc acetate dihydrate [Zn(COOCH$_3$)$_2$ 2(H$_2$O)], lanthanum(III)acetate sesquihydrate [La(CH$_3$COO)$_3$ 1.5(H$_2$O)], cerium(III)acetate tetrahydrate [Ce(CH$_3$COO)$_3$ (30x70) Springer
4H2O), and dysprosium(III)acetate tetrahydrate [Dy(CH3COO)3 4H2O], were of high purity (Sigma-Aldrich 99% purity) and were used as such, without any further purification. Distilled water was used as the reaction medium and diethylamine as the reducing as well as stabilizing agent. To begin with, undoped ZnO nanoparticles were synthesized by taking 0.5 M zinc acetate solution in a beaker at 60 °C and adding 5 ml of diethylamine slowly to it. The solution was stirred at 60 °C for 30 min followed by heating at 180 °C. The resulting powders were obtained by centrifugation and were annealed at 500 °C in a muffle furnace for 1 h.

In order to obtain the La, Ce, and Dy-co-doped samples, i.e., Zn0.97La0.01Ce0.01Dy0.01O, Zn0.94La0.02Ce0.02Dy0.02O, Zn0.91La0.03Ce0.03Dy0.03O, Zn0.88La0.04Ce0.04Dy0.04O, and Zn0.85La0.05Ce0.05Dy0.05O, the dopant ion salts were used to prepare salt solutions in distilled water with concentrations varying from 0.01 M to 0.05 M. These solutions were then added to 0.5 M ZnO solution under stirring at 60 °C. Five milliliters of diethylamine was added to this solution dropwise. The heating was further continued for 1 h and the resulting powders were centrifuged and cleaned with ethanol and annealed at 500 °C for each molar concentration from 0.01 M to 0.05 M. The standard conditions and molarities for the synthesis of La, Ce, and Dy-co-doped ZnO nanoparticles are depicted in Table 1.

The structural properties of nanoparticles were examined using X-ray diffractometer with CuKα target (k = 1.54052 Å). The radiation was over the range of 2θ from 10–90° and step size was 0.01. The morphological features of undoped ZnO and La, Ce, and Dy-co-doped ZnO nanoparticles were observed under SEM. For PL study, Horiba LabRam spectrometer with an excitation source of 325 nm (wavelength) and an accumulation time of 2 s was used. Optical studies were done using DRS, UV–VIS–NIR spectrometer at a normal incidence of powder samples (USB 2000 and deuterium halogen power source DH-2000 Micropack; Ocean Optics).

### Structural Analysis

Figure 1a reveals the XRD pattern of undoped and La, Ce, and Dy-co-doped ZnO nanoparticles with concentrations (Zn0.97La0.01Ce0.01Dy0.01O, Zn0.94La0.02Ce0.02Dy0.02O, Zn0.91La0.03Ce0.03Dy0.03O, Zn0.88La0.04Ce0.04Dy0.04O, and Zn0.85La0.05Ce0.05Dy0.05O). XRD analysis shows all the nanoparticles formed are of hexagonal wurtzite phase as per The International Centre for Diffraction Data (ICDD) database number 01–070-8072. The sharpness of all the peaks indicated purely crystalline nature of the nanoparticles. Further analysis revealed there were no secondary peaks other than ZnO indicating that all the samples

### Photocatalytic Activity Measurement

To measure the photocatalytic activity of undoped and La, Ce, and Dy-co-doped ZnO nanoparticles, 40 mg of nanoparticle powder was weighed. In a 250-ml beaker, 10 ml of 10 ppm Rhodamine B dye solution was taken, and to this 30 ml of distilled water was added. Finally the weighed nanoparticle powder was added to this 40 ml dye solution. This solution was wrapped, kept in dark and stirred for half an hour to disperse the photocatalyst nanoparticles and establish adsorption–desorption equilibrium. Afterward, the solution was irradiated with UV light in the photocatalytic reactor (M/S Technistro, Nagpur, Maharashtra, India) fitted with high-pressure mercury lamp with capacity 450 W (operating voltage, 110–220 V), while the stirring was continued. A 3 ml aliquot was taken at an interval of 10 min and immediately centrifuged to remove catalyst. Absorbance of the samples was measured using UV–VIS spectrometer (Perkin Elmer Lambda 35) run between 400–600 nm. A decrease in absorbance and removal of dye color confirmed the degradation of Rhodamine B dye with undoped and La, Ce, and Dy-co-doped ZnO as photocatalyst.

### Results and Discussion

#### Structural Analysis

Table 1 Standard conditions for synthesis of La, Ce, and Dy-co-doped ZnO nanoparticles x = (0.00–0.05)

| Mole fraction (La, Ce and Dy) | Zinc acetate (M) | Lanthanum acetate (M) | Cerium acetate (M) | Dysprosium acetate (M) | Diethylamine (CC) |
|------------------------------|------------------|-----------------------|-------------------|------------------------|------------------|
| 0.00                         | 0.5              | 0.000                 | 0.000             | 0.000                  | 0.5              |
| 0.01                         | 0.5              | 0.003                 | 0.003             | 0.003                  | 0.5              |
| 0.02                         | 0.5              | 0.006                 | 0.006             | 0.006                  | 0.5              |
| 0.03                         | 0.5              | 0.01                  | 0.01              | 0.01                   | 0.5              |
| 0.04                         | 0.5              | 0.013                 | 0.013             | 0.013                  | 0.5              |
| 0.05                         | 0.5              | 0.016                 | 0.016             | 0.016                  | 0.5              |
formed were pure phase. The ionic radius of host ion \( \text{Zn}^{2+} \) (0.72 Å) is small as compared to the dopant ions, i.e., \( \text{La}^{3+} \) (1.06 Å), \( \text{Ce}^{3+} \) (1.03 Å) and \( \text{Dy}^{3+} \) (0.91 Å) which leads to distortion in the ZnO lattice and also there is a shift toward lower angle in the doped samples, confirming substitutional doping of La, Ce, and Dy-co-dopants in ZnO matrix which is shown in Fig. 1b. The formulae used for the calculation of lattice parameters and crystallite size, respectively, are listed below and the numeric values of same are given in Table 2. Mismatch of ionic radii of host \( \text{Zn}^{2+} \) ion and dopant ions leads to an increase in bond length which gets reflected in increased values of lattice constants \( a \) and \( c \) as shown in Table 2.

\[
a = \frac{\lambda}{\sqrt{\sin \theta}} \quad \text{(1)}
\]

\[
c = \frac{\lambda}{\sin \theta} \quad \text{(2)}
\]

In the above formulae \( \lambda \) represents the wavelength of target used in the X-ray diffractometer, and its value is 1.5406 Å. \( \theta \) and \( K \) represent the diffraction angle and the shape factor, respectively, \( D \) is crystallite size and \( \beta \) denotes full width half maximum. The crystallite size decreases from 47 nm in case of undoped ZnO to around 35 nm in case of doped nanoparticles, and hence dopant concentration restricts the growth of nanoparticles in doped samples and which was confirmed and explained using scanning electron microscopy SEM.

### Morphological Studies

The SEM micrographs of undoped and La, Ce, and Dy-co-doped ZnO are shown in Fig. 2(a–f). It can be clearly seen from the SEM micrographs that the SEM results are in concurrence with the XRD results. The grain size was

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**Table 2** Calculated lattice parameters and crystallite size of undoped and La, Ce, and Dy-co-doped ZnO nanoparticles

| Sample | Lattice parameters | Crystallite size(nm) |
|--------|-------------------|---------------------|
|        | \( a(\text{Å}) \) | \( c(\text{Å}) \) |              |
| Undoped | 3.196             | 5.204               | 47           |
| 0.01 M La, Ce, and Dy-co-doped ZnO | 3.240 | 5.210 | 38 |
| 0.02 M La, Ce, and Dy-co-doped ZnO | 3.243 | 5.218 | 37 |
| 0.03 M La, Ce, and Dy-co-doped ZnO | 3.247 | 5.223 | 36 |
| 0.04 M La, Ce, and Dy-co-doped ZnO | 3.250 | 5.230 | 36 |
| 0.05 M La, Ce, and Dy-co-doped ZnO | 3.253 | 5.241 | 35 |
estimated using SEM and was found to be approximately around 50 nm. Increase in dopant concentration leads to decrease in grain size. Ionic radii of dopant ions La$^{3+}$ (1.06 Å), Ce$^{3+}$ (1.03 Å) and Dy$^{3+}$ (0.91 Å) are quite large as compared to the host Zn$^{2+}$ ion, i.e., (0.72 Å). This mismatch in ionic radii leads to lattice strain and eventually
a decreased grain size in case of doped nanoparticles. It can be observed from the SEM micrographs that on increasing the dopant concentration the morphology of the nanoparticles eventually becomes flower like. This phenomenon can be credited to the Ce$^{3+}$ ion doping which plays a pivotal role in capping the nanoparticles after nucleation [46]. The Ce$^{3+}$ ions cause steric hindrances in presence of a strongly absorbed reducing agent—diethylamine, which leads to formation of flower-like structure in case of La, Ce, and Dy-co-doped ZnO nanoparticles. This can be further explained with the help of growth and nucleation of nanoparticles. A precursor initiates the formation of seed nuclei which then grow to form rods by Ostwald ripening effect, in which larger grains grow at the expense of smaller crystals. Solvent facilitates this process and various subunits formed are connected by the orientation attachment process leading to flower like morphology [47].

**Compositional Studies**

Energy-dispersive spectroscopy (EDS) was used to confirm the incorporation of dopant ions into the host matrix. Figure 2g and h shows the chemical composition of undoped and La, Ce, and Dy-co-doped (Zn$_{0.88}$La$_{0.04}$Ce$_{0.04}$Dy$_{0.04}$O) ZnO nanoparticles. In case of undoped ZnO sample, only the presence Zn and O was noticed, while in case of La, Ce, and Dy-co-doped sample the presence of dopant ions La, Ce, and Dy was noticed in addition to the Zn which confirmed the inclusion of all three dopants into ZnO matrix.

**Photoluminescence Studies**

Important properties of semiconductors like bandgap, energy levels, chemical composition, and type of impurity can be extensively studied with the help of photoluminescence (PL). The PL spectra of undoped and La, Ce, and Dy-co-doped ZnO nanoparticles are shown in Fig. 3a. The spectra were obtained by exciting the sample at a wavelength of 325 nm. The PL spectrum of pure or undoped ZnO depicts two prominent emission peaks at 390 nm and 710 nm. The first prominent peak at 390 nm corresponds to the UV region and is due to near band edge emission caused by the recombination of free and bound exciton pairs. The second peak at 710 nm corresponds to the near infrared region and is possibly ascribed to surface plasma resonance [48]. Figure 3a shows that La, Ce, and Dy co-doping has two important influences on the photoluminescence emission peaks in UV region that is decrease in intensity of emission peaks and shifting of emission peaks toward the higher wavelength. A decrease in intensity can be attributed to the transfer of energy from host ZnO to dopants La, Ce, and Dy which confirms perfect substitution of dopants into the host matrix. A decrease in peak intensity and consequent decrease in energy also indicates delayed recombination with increase in dopant concentration. This pertains to the fact that increased dopant concentration leads to surface bound states acting as trap states resulting in nonradiative relaxation. The PL intensity depends on the distance between these trap states and their center-to-center interaction. The spectral overlap between the wave functions of these states leads to dissipation of energy in non-radiative manner and consequent decrease in

![Fig. 3](image)

- **Fig. 3** a Room temperature PL spectrum of undoped and La, Ce, and Dy-co-doped ZnO nanoparticles (Zn$_{0.97}$La$_{0.01}$Ce$_{0.01}$Dy$_{0.01}$O, Zn$_{0.94}$La$_{0.02}$Ce$_{0.02}$Dy$_{0.02}$O, Zn$_{0.91}$La$_{0.03}$Ce$_{0.03}$Dy$_{0.03}$O, Zn$_{0.88}$La$_{0.04}$Ce$_{0.04}$Dy$_{0.04}$O & Zn$_{0.85}$La$_{0.05}$Ce$_{0.05}$Dy$_{0.05}$O) b Expanded UV region of the spectrum showing red shift in wavelength with increase in concentration of dopants
energy [49]. La, Ce, and Dy co-doping also leads to shifting of the peak in UV region toward the visible region of spectrum as shown in Fig. 3b. This is a very important consequence which can lead to better utilization of the solar energy and pave way for excellent optoelectronic applications. This red shift can be attributed to the creation of electronic states near the conduction band of ZnO due to presence of dopants, which also leads to narrowing of bandgap of ZnO as has already been reported in Ce-doped nitrides [50]. Narrowing of bandgap can further be credited to the narrow optical transitions within spin orbital levels due to tailoring of conduction and valence bands caused by dopant-induced potential fluctuations [51]. As the electronegativities of the dopant ions La$^{3+}$ (1.1), Dy$^{3+}$ (1.22), and Ce$^{3+}$ (1.12) are less than the electronegativity of host Zn$^{2+}$ (1.65), the cumbolic interaction between electrons–holes pairs bound by isoelectronic levels formed by La, Ce, and Dy generates acceptor-bound excitation pair. This leads to charge transfer between conduction band of ZnO and different states of dopants, causing a red shift which consequently narrows the bandgap.

**Photocatalytic Studies**

The photocatalytic activities of undoped and La, Ce, and Dy-co-doped ZnO nanoparticles were analyzed by observing the degradation of Rhodamine B dye under UV light irradiation. The experiment was performed at room temperature and neutral pH. The 10 ppm dye solution with 40 mg catalyst powder was initially stirred in dark for 30 min and absorbance measured after that was taken as dark study. Figure 4a–f reveals the degradation of Rhodamine B dye with ZnO and La, Ce, and Dy-co-doped ZnO as nanophotocatalysts within reaction time from 0 to 60 min, where 0 min in each case is the dark study that is before illumination with UV light. The degradation is confirmed as the absorbance of dye decreases with an increase in concentration of dopants and reaction time. We observed the fastest and most efficient degradation with La, Ce, and Dy-co-doped ZnO having concentration Zn$_{0.85}$La$_{0.05}$Ce$_{0.05}$Dy$_{0.05}$O. The photocatalytic performance of undoped and La, Ce, and Dy-co-doped ZnO nanoparticles was mathematically evaluated by taking the plot between Ct/Co and irradiation time (t), where Co is the initial dye concentration and Ct is the residual dye concentration after a time interval t as shown in Fig. 5a. The degradation of Rhodamine B dye roughly obeys pseudo-first-order kinetics for low concentration of dyes [52].

$$\ln \left( \frac{C_t}{C_0} \right) = K \times t$$  \hspace{1cm} (4)

where $K$ represents the constant-kinetic parameter and is different for different photocatalysts. The value of constant K can be found by linear fitting the slope of graph obtained between In (Ct/Co) and irradiation time t as is shown in Fig. 5b. The values of K obtained in this case were 0.0247 S$^{-1}$, 0.0408 S$^{-1}$, 0.0407 S$^{-1}$, 0.055 S$^{-1}$, 0.058 S$^{-1}$, and 0.060 S$^{-1}$ for undoped and La, Ce, and Dy-co-doped ZnO nanoparticles with concentrations viz (Zn$_{0.97}$La$_{0.02}$Ce$_{0.01}$Dy$_{0.00}$O, Zn$_{0.94}$La$_{0.02}$Ce$_{0.02}$Dy$_{0.00}$O, Zn$_{0.92}$La$_{0.03}$Ce$_{0.03}$Dy$_{0.00}$O, Zn$_{0.88}$La$_{0.04}$Ce$_{0.00}$Dy$_{0.02}$O and Zn$_{0.85}$La$_{0.05}$Ce$_{0.05}$Dy$_{0.05}$O), respectively. The value of K was found to be highest in case of highest doping concentration, i.e., Zn$_{0.85}$La$_{0.05}$Ce$_{0.05}$Dy$_{0.05}$O. The degradation efficiency was further studied by calculating the degradation percentage using the formula given below:

$$\% D = \left(1 - \frac{C_t}{C_0}\right) \times 100$$  \hspace{1cm} (5)

where $\% D$ is the degradation percentage, $C_o$ is the initial concentration of dye, and Ct is the concentration of dye after interval t. The degradation percentage was found to be highest (93%) for La, Ce, and Dy-co-doped ZnO nanoparticles with concentration Zn$_{0.85}$La$_{0.05}$Ce$_{0.05}$Dy$_{0.05}$O. This is depicted graphically in Fig. 5c.

Enhanced photocatalytic activity of ZnO nanoparticles with trivalent rare earth doping can be explained by investigating the degradation mechanism of Rhodamine B dye as follows. The semiconductor nanoparticles to be investigated as photocatalysts are initially excited with photons having energy greater than their bandgap, i.e., (hv > bandgap). This excitation generates electron–hole pairs on the surface of the nanoparticle. This trapping of photogenerated electrons and holes is the rate determining step in photocatalysis reaction. The 4f configuration of rare earth dopants also plays a pivotal role in generation, delayed recombination, and delayed charge transfer of electron hole pairs. La$^{4+}$, Ce$^{4+}$, and Dy$^{4+}$ act as scavengers for the electrons from conduction band as these are stronger Lewis acids compared to O$_2$ and hence better at trapping the electrons and holes. The electrons trapped by the dopants are transferred oxidatively to the surface adsorbed oxygen to produce the superoxide radical (*O$_2^-$). The electrons and holes generated by high energy photons can easily recombine and dissipate the energy, which prevents their efficient utilization. The recombination of photogenerated electrons and holes can be prevented in the presence of defect states. In the present work, singly oxygen vacancies (Vo$^+$) act as trap states to enhance the separation between photogenerated electrons and holes. The singly oxygen vacancy acts as electron donor to become charged oxygen vacancy which then acts as trap for photogenerated holes and prevents recombination. This charged oxygen vacancy on reaction with the hydroxyl ion
Fig. 4 UV Vis Absorbance spectral changes of Rhodamine B dye solution during photocatalytic degradation with undoped and La, Ce, and Dy co-doped ZnO nanoparticles under UV irradiation at different time intervals. a Undoped ZnO, b Zn$_{0.97}$La$_{0.01}$Ce$_{0.01}$Dy$_{0.01}$O, c Zn$_{0.94}$La$_{0.02}$Ce$_{0.02}$Dy$_{0.02}$O, d Zn$_{0.91}$La$_{0.03}$Ce$_{0.03}$Dy$_{0.03}$O, e Zn$_{0.88}$La$_{0.04}$Ce$_{0.04}$Dy$_{0.04}$O, f Zn$_{0.85}$La$_{0.05}$Ce$_{0.05}$Dy$_{0.05}$O.
(OH\textsuperscript{\textastern}) forms hydroxyl radical (OH\textsuperscript{\textastern}). This can be summarized as:

\[ \text{Incident photons} + \text{ZnO} \rightarrow \text{electrons (e}^{-}\text{) + holes (h}^{+}\text{)} \]

\[ \text{Ce}^{4+} + \text{e}^{-} \rightarrow \text{Ce}^{3+} \]

\[ \text{Dy}^{4+} + \text{e}^{-} \rightarrow \text{Dy}^{3+} \]

\[ \text{e}^{-} + \text{O}^{2} \rightarrow \text{O}_{2}^{\text{\textastern}} \text{(superoxide)} \]

\[ \text{Vo}^{+} + \text{h}^{+} \rightarrow \text{Vo}^{2+} \]

\[ \text{Vo}^{2+} + \text{OH}^{-} \rightarrow \text{Vo}^{+} + \text{OH} \text{ (hydroxyl radical)} \]

\[ \text{Zn}_{0.01}\text{La}_{0.03}\text{Ce}_{0.01}\text{Dy}_{0.05}\text{O}, \text{Zn}_{0.04}\text{La}_{0.02}\text{Ce}_{0.02}\text{Dy}_{0.02}\text{O}, \text{Zn}_{0.03}\text{La}_{0.03}\text{Ce}_{0.03}\text{Dy}_{0.03}\text{O}, \text{Zn}_{0.04}\text{La}_{0.04}\text{Ce}_{0.04}\text{Dy}_{0.04}\text{O} \& \text{Zn}_{0.05}\text{La}_{0.05}\text{Ce}_{0.05}\text{Dy}_{0.05}\text{O} \]

\[ \text{Zn}_{0.88}\text{La}_{0.04}\text{Ce}_{0.04}\text{Dy}_{0.04}\text{O} \& \text{Zn}_{0.85}\text{La}_{0.05}\text{Ce}_{0.05}\text{Dy}_{0.05}\text{O} \]

Fig. 5 a Photocatalytic degradation of Rhodamine B dye solution undoped and La, Ce, and Dy-co-doped ZnO nanoparticles (Zn\textsubscript{0.97}, La\textsubscript{0.01}, Ce\textsubscript{0.01}, Dy\textsubscript{0.01}O, Zn\textsubscript{0.94}, La\textsubscript{0.02}, Ce\textsubscript{0.02}, Dy\textsubscript{0.02}O, Zn\textsubscript{0.93}, La\textsubscript{0.03}, Ce\textsubscript{0.03}, Dy\textsubscript{0.03}O, Zn\textsubscript{0.90}, La\textsubscript{0.04}, Ce\textsubscript{0.04}, Dy\textsubscript{0.04}O & Zn\textsubscript{0.88}, La\textsubscript{0.05}, Ce\textsubscript{0.05}, Dy\textsubscript{0.05}O) under UV irradiation at different time intervals.

b Reaction kinetics of photolytic catalytic degradation with undoped ZnO nanoparticles and La, Ce, and Dy-co-doped ZnO nanoparticles (Zn\textsubscript{0.97}, La\textsubscript{0.01}, Ce\textsubscript{0.01}, Dy\textsubscript{0.01}O, Zn\textsubscript{0.90}, La\textsubscript{0.02}, Ce\textsubscript{0.02}, Dy\textsubscript{0.02}O, Zn\textsubscript{0.88}, La\textsubscript{0.03}, Ce\textsubscript{0.03}, Dy\textsubscript{0.03}O, Zn\textsubscript{0.85}, La\textsubscript{0.04}, Ce\textsubscript{0.04}, Dy\textsubscript{0.04}O & Zn\textsubscript{0.88}, La\textsubscript{0.05}, Ce\textsubscript{0.05}, Dy\textsubscript{0.05}O) under UV irradiation at different time intervals.

c Photocatalytic degradation percentage of Rhodamine B dye solution with undoped ZnO and La, Ce, and Dy-co-doped ZnO nanoparticles (Zn\textsubscript{0.97}, La\textsubscript{0.01}, Ce\textsubscript{0.01}, Dy\textsubscript{0.01}O, Zn\textsubscript{0.90}, La\textsubscript{0.02}, Ce\textsubscript{0.02}, Dy\textsubscript{0.02}O, Zn\textsubscript{0.88}, La\textsubscript{0.03}, Ce\textsubscript{0.03}, Dy\textsubscript{0.03}O, Zn\textsubscript{0.85}, La\textsubscript{0.04}, Ce\textsubscript{0.04}, Dy\textsubscript{0.04}O & Zn\textsubscript{0.88}, La\textsubscript{0.05}, Ce\textsubscript{0.05}, Dy\textsubscript{0.05}O) under UV irradiation at different time intervals.

\[ \text{O}_{2}^{-} + \text{2H}^{+} \rightarrow \text{2(OH)} \]

Organic pollutant + OH\textsuperscript{\textastern} + O\textsubscript{2} → CO\textsubscript{2} + H\textsubscript{2}O + degraded products

Oxygen vacancies do not only trap holes, and they also help in adsorbing oxygen and hence further enhance photocatalysis [53].

The efficiency of any photocatalyst depends on a number of factors which include number of charge carriers on the surface, and recombination rate of the electron–hole pairs generated upon incidence of high energy photon. In the present work, rare earth doping in ZnO has been utilized to increase its photocatalytic activity many folds as compared to the undoped ZnO. The reason for this can be
credited to loading of charge carriers on the surface as a consequence of decrease in size and increase in surface area on doping and presence of oxygen vacancies in the bandgap of ZnO due to trivalent rare earth doping. Photoluminescence (PL) studies Fig. 3a–b reveal that the trivalent rare earth doping causes the shifting of absorption edge toward the visible region and narrowing of bandgap. Both these effects can lead to better utilization of solar energy and hence more efficient photocatalysis. Further PL spectrum reveals incorporation of additional levels in the bandgap of ZnO upon rare earth doping which also delays the recombination of charge carriers leading to efficient photocatalysis. This red shift in absorption edge and bandgap narrowing are also confirmed by diffuse reflectance studies (DRS).

**Optical Studies, Diffuse Reflectance Studies—(DRS)**

Figure 6a depicts the diffuse reflectance spectra of undoped and Zn$_{0.97}$La$_{0.01}$Ce$_{0.01}$Dy$_{0.01}$O, Zn$_{0.91}$La$_{0.03}$Ce$_{0.03}$Dy$_{0.03}$O, & Zn$_{0.85}$La$_{0.05}$Ce$_{0.05}$Dy$_{0.05}$O samples, respectively. Red shift along with narrowing of bandgap can be attributed to the creation of additional trap or defect states in the bandgap of ZnO and formation of oxygen vacancies due to doping. These lead to increase in average atomic distance and hence decrease in bandgap [58].

$$F(R) = \frac{(1 - R)^2}{2R}$$

where $F$ is the Kubelka–Munk function and $R$ represents the reflectance, is calculated using the above formula and then a plot is drawn between $[F(R)/hv]^2$ vs hv. Here $h$ is the Planck’s constant and $v$ is the frequency, $v = 1/\lambda$ and wavelength $\lambda$ is found from x-axis of graph shown in Fig. 6a. The lines in Fig. 6b show the extrapolation of linear portion of plot $F(R)/hv)^2$ vs hv. The points at which these lines touch the x-axis give us the bandgap values. The bandgap of undoped ZnO was found to be 3.11 eV. For doped samples, a decrease in bandgap was observed. Band gap values of 3.06 eV, 3.04 eV and 2.85 eV were found for Zn$_{0.97}$La$_{0.01}$Ce$_{0.01}$Dy$_{0.01}$O, Zn$_{0.91}$La$_{0.03}$Ce$_{0.03}$Dy$_{0.03}$O, and Zn$_{0.85}$La$_{0.05}$Ce$_{0.05}$Dy$_{0.05}$O samples, respectively.
Conclusion

Pure and La, Ce, and Dy-co-doped ZnO nanoparticles were successfully prepared using a facile and cost effective approach of co-precipitation. Successful formation of nanoparticles was confirmed by XRD. A slight distortion in XRD pattern of doped samples was found due to ionic radii mismatch between host and dopant ions. Average particle size was found to be around 35 nm. Morphology was evaluated using SEM, and the doped nanoparticles were found to have a flower-like morphology. Photoluminescence PL studies revealed a red shift in absorption edge and narrowing of bandgap. Tunable band gap makes the doped nanoparticles excellent candidates for optoelectronic applications. Photocatalytic studies confirmed an enhanced and optimized photo catalytic performance in case of La, Ce, and Dy-co-doped samples due delayed recombination of photogenerated charge carriers. The creation of additional levels in the band gap of ZnO together with increased surface oxygen vacancies and charge transfer further contributed to the improved photocatalytic performance.

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