Improved Luminescence and Photocatalytic Proprieties of Sm$^{3+}$-doped ZnO Nanoparticles Via Modified Sol-Gel Route: An Unified Experimental and DFT+U Approach

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Abstract

In the current study, a modified sol-gel route was followed to produce undoped and Sm$^{3+}$ doped (1, 3 and 5 mol %) nanoparticles. The study of opto-structural properties of Sm$^{3+}$ doped NPs was carried out both experimentally and theoretically. Complete dissolution of Sm$^{3+}$ ions into the ZnO lattice was obvious from XRD analysis. Morphological evolution with doping was studied using FESEM and TEM. XPS was carried out to confirm the presence of Sm$^{3+}$ on the surface of the doped NPs. Increasing dopant quantity resulted in a red shift of the NPs along with a reduction in band gap with increasing absorption in the visible range, and a minimum of 3.18 eV of optical band gap for Zn$_{0.97}$Sm$_{0.03}$O was found. Photoluminescence spectroscopy revealed a drop in the recombination rate of electron-hole with increasing doping till 3 mole %, followed by an increase for Zn$_{0.95}$Sm$_{0.05}$O. Photogenerated electron-hole pair recombination was revealed by the orange band in the luminescence spectra. Theoretical analysis was also carried out with density function theory (DFT). This work also unfolds the fundamental understanding of the structural properties of the synthesized NPs to enhance photocatalytic activity successfully. Later, photocatalytic activity for the optimum composition i.e., 3 mole percent, was assessed experimentally.

1 Introduction

ZnO nanoparticles (NPs) have gained a lot of popularity in recent years in applications such as UV lasers, photo detectors, gas sensors and photocatalysis which is attributed to the wide direct band gap along with large exciton binding energy [1–4]. Moreover, ZnO nanoparticles have an edge over other semiconductors in optoelectronics due to their non-toxicity, durability along with efficient absorption of the broad solar spectra [5]. Diverse morphology i.e. nanowires, nanorods, nanobelts, nanotubes, nanocapsules and nanohelices has gained considerable popularity among researchers as morphology and sizes play a pivotal role to optimize the optoelectronic properties of ZnO NPs[6, 7]. Additionally, optoelectronic and photocatalytic properties of ZnO NPs can be enhanced through controlled band gap tuning[8–10]. Doping with rare earth elements is a promising approach to tune band gap of ZnO to make it favorable for optoelectronic applications[11–17]. Moreover, rare earth ions delay the recombination of photogenerated charges and thus photocatalytic performance is enhanced by active charge trapping[18]. Furthermore, rare-earth doped ZnO NPs modulate visible region emission because of their unique 4f electronic configuration effectively making them a promising candidate for multicolored LEDs[19–21]. Among rare-earth elements, samarium (Sm) has gained considerable attention among researchers in recent times, because Sm$^{3+}$ ions act as effective luminescent and trapping sites of the charge carriers in ZnO nanoparticles which makes them suitable for optoelectronic and photocatalytic applications[22–24]. Hydrothermal, sol-gel, gaseous phase deposition, successive ionic layer adsorption and reaction (SILAR) method, etc. methods are widely used to synthesize ZnO NPs[25–30]. A pivotal role is played by the synthesizing route to control the morphology, crystallinity and optoelectronic characteristics of the nanoparticles[31]. The modified sol-gel approach has numerous benefits compared to other existing processes, including lower processing costs, simplicity, lower operating temperatures, and improved
control over chemical homogenization of nanoparticles[32]. Here, as the authors believe, for the very first time Sm$^{3+}$ was incorporated in ZnO NPs by this route followed by the experimental study of opto-structural and photocatalytic properties of the synthesized NPs. The DFT study has also been carried out as it has proved to be instrumental in revealing the underlining correlation between structural, opto-electronic properties of rare-earth modified ZnO NPs[33].

2 Methodology

2.1 Synthesis of ZnO NPs Doped with Sm$^{3+}$

The chemical reagents used in this research were analytical grade. The nanoparticles were prepared by using a required amount of Zinc nitrate hexahydrate and samarium nitrate hexahydrate as precursors. To produce the solution of the salts, de-ionized water was used before the addition of the stabilizer i.e., ethylene glycol. The solution was stirred for an hour while maintaining a temperature of 80°C. The clear homogeneous solution was then supplemented with a double molar amount of citric acid ($C_6H_8O_7$) compared to zinc precursor. The solution was stirred vigorously for two more hours at constant temperature and speed. Meanwhile, the formation of thick gel had occurred and the gel was dried at 120°C. Powders were calcined at 500°C for a couple of hours. Finally, crushed fine powders were obtained by grinding the calcined powders.

2.2 Characterization

The crystal structure of the prepared nanoparticles was investigated by obtaining the powder X-ray diffraction patterns by Philips x-ray diffractometer [PW 3040-X'Pert PRO]. Field emission scanning electron microscopy (FE SEM: JEOL, JSM, 7600F) and transmission electron microscopy (Talos F200X TEM, Thermo Fisher Scientific, USA) were employed to analyze particle morphology and size. SHIMADZU UV 2600 Spectrophotometer was utilized to measure absorbance and diffusion reflectance spectra, with the baseline adjusted with BaSO$_4$ and SHIMADZU RF-6000 Spectro-fluorophotometer (excitation wavelength 200 nm) was employed to examine the photoluminescence (PL) spectra. K-Alpha thermoscientific XPS-spectrometer was used to reveal the chemical states of the species.

2.3 Photocatalytic Degradation

The photocatalytic performance of the NPs under UV light was evaluated by the photodegradation of Rhodamine B (RhB) dye in an aqueous solution of basic medium (pH ~ 10). A solar simulator (Hamamatsu L8288, 500 W) was used to generate solar light and a UV pass filter was used to obtain UV light for the degradation[34–37]. The degradation of the dye under the illumination with the presence of the NPs was measured by the intensity of the absorbance peak of the UV-vis spectroscopy. The absorbance measurement was carried out for 180 min at a 30 min intervals. The stability and reusability test of the nanoparticles was carried out by 4 successive runs. The remaining NPs were extracted from the solution after each cycle to use as photocatalysis in the next photodegradation cycle.

2.4 Computational Analysis
All calculations presented here are based on density functional and done within the project-augmented method. For exchange-correlations, the Perdew-Burke-Ernzerhof (PBE) function was used. In the Generalized gradient approximation (GGA) potential were used for valance electrons of Zn (orbitals: 3d, 4s, 4p), O (orbitals: 2s, 2p) and Sm (orbitals: 4f, 5d) [38]. All the calculations were performed using Quantum Espresso simulation package simulation [39, 40]. The Hubbard-based DFT + U correction scheme was utilized to counter the problem of underestimating band gaps of the standard DFT[41]. This type of correction is used to understand the behavior of compounds made with transition metals [42, 43]. In the DFT (PBE) +U calculations for zinc orbital d, $U_{\text{eff}} = 10.8 \text{eV}$ and for oxygen orbital p, $U_{\text{eff}} = 7 \text{eV}$ were used that computed the bandgap of 3.24 eV which is almost similar to the experimentally measured bandgap of pure ZnO. For the f orbital of Sm, we used $U_{\text{eff}} = 7 \text{eV}$. Rietveld refinement provides the primary structures of the pristine and Sm$^{3+}$ doped ZnO NPs. ZnO has a wurtzite hexagonal structure whose unit cell consists of 2 Zinc and 2 Oxygen atoms. However, for simulating the doped systems, supercells are essential [44, 45]. For structural relaxation plane wave basis was used and pully stress was avoided by energy cutoff at 520 eV. In self-consistent field calculations, between two successive steps the energy convergence benchmark was fixed at 10-7 eV. Relaxation of atomic positions was done to bring Hellmann – Feynman forces below 0.01 eV/Å. Monkhorst-Pack of 12×12×6 scheme and $\sigma = 0.05$ sigma value of Gaussian Smearing was used to integrate the Brillouin zone to relax the unit cell. For accurate calculations, tetrahedron smearing method was used where the k-points mesh was 18×18×10. The spin-polarized method was followed for all calculations.

3 Results And Discussion

3.1 X-ray Diffraction

X-ray diffraction data of Zn$_{1-x}$Sm$_x$O ($x = 0.01, 0.03$ and $0.05$) NPs are illustrated in figure 1. The data is in accordance with JCPDS card 36-1451 which confirms the hexagonal wurtzite structure of all the nanoparticles [46]. Diffraction peaks of impurity phases such as Sm or Sm$_2$O$_3$ were absent which ensures the complete incorporation of Sm$^{3+}$ into the matrix. On doping with Sm$^{3+}$ ions, crystallinity was decreased which is obvious from the reduced diffraction peak intensity. As Zn$^{2+}$ ions ($R_{\text{Zn}^{2+}}$=0.74 Å) were substituted by Sm$^{3+}$ ions ($R_{\text{Sm}^{3+}}$=1.09 Å), lattice disorder was generated leading to a decrease in crystallinity [19]. Sm$^{3+}$ doping expands the lattice cell as its radius is larger than that of Zn$^{2+}$, and therefore, the diffraction peak of the (002) plane shifts subtly towards a lower diffraction angle[47].

For all the planes, Figure 1 shows an increase of full-width half maximum (FWHM) values, which indicates that crystallite size was decreased with increasing dopant amount[48]. Moreover, micro-stain was induced on doping which resulted in lattice disorder and stress generation[49]. Table 1 shows strain and crystallite size values derived from Williamson-Hall (W-H) equation[50−52]. For pristine ZnO average crystallite size was 31.2 nm whereas it was only 11.6 nm for 5 mole percent doping. On the nanoparticle’s surface Zn–O–Sm formation impedes further crystal grain growth and thus, decreases the crystallite size [53]. Using Scherrer’s equation, the crystallite size was again calculated and a similar trend was
observed. Microstrain increased when dopant was added and maximum microstrain was observed for Zn$_{0.95}$Sm$_{0.05}$O. Rietveld analysis was done using X’Pert HighScore Plus and the results were summarized in Table 2. Phase purity along with an increase of c/a value from 1.6024 to 1.6037 is confirmed by Rietveld analysis which further supports the low-angle peak shift.

### Table 1

| Element          | Crystallite Size (nm) | Strain, ε * 10$^{-3}$ (W-H plots) |
|------------------|-----------------------|------------------------------------|
|                  | W-H plots | Scherrer’s Equation |                      |
| ZnO              | 31.2      | 28.4                | 0.82                  |
| Zn$_{0.99}$Sm$_{0.01}$O | 22.5      | 18.1                | 1.95                  |
| Zn$_{0.97}$Sm$_{0.03}$O | 16.9      | 15.2                | 2.16                  |
| Zn$_{0.95}$Sm$_{0.05}$O | 11.6      | 12.3                | 3.04                  |

### Table 2

| Element          | Lattice Parameters (Å) | Profile Factor, $R_p$ | Weighted Profile Factor, $R_{wp}$ | Goodness of Fit |
|------------------|------------------------|-----------------------|-----------------------------------|-----------------|
|                  | a  | c  | c/a |                |                      |                        |
| ZnO              | 3.2495 | 5.2072 | 1.6024 | 6.53 | 8.84 | 1.79 |
| Zn$_{0.99}$Sm$_{0.01}$O | 3.2502 | 5.2089 | 1.6026 | 7.04 | 9.32 | 1.92 |
| Zn$_{0.97}$Sm$_{0.03}$O | 3.2493 | 5.2103 | 1.6035 | 5.75 | 7.63 | 1.56 |
| Zn$_{0.95}$Sm$_{0.05}$O | 3.2483 | 5.2092 | 1.6037 | 5.08 | 6.44 | 1.31 |

### 3.2 Morphology of Nanoparticles

With increasing doping amount, a smaller-size morphology was evolved compared to pristine ZnO nanoparticles (figure 2). Hexagonal nanoparticles for undoped ZnO were observed which is evident from figure 2a. When Sm$^{3+}$ replaces Zn$^{2+}$ in nanoparticles, it induces a positive charge, which affects the morphology. Nanoparticles’ size showed a decrease when dopant amount raises from 1 mole to 3 mole percent as particle growth is inhibited on doping (figure 2(b-c)). An increase in the size of nanoparticles was observed for further doping and the shape of the nanoparticles become near-spherical along with agglomerated nanoparticles (figure 2d).

The variation in particle size with doping was also clearly visible in TEM images (figure 3). The particle size of hexagonal-shaped undoped ZnO NPs varied from 40 to 60 nm, with occasional outliers (figure 3(a-b)). In Zn$_{0.97}$Sm$_{0.03}$O nanoparticles, small-sized homogeneous nanoparticles ranging from 20 to 25 nm were observed (figure 3(a-b)). The findings are analogous to those of XRD and FESEM.
3.3 UV-vis Spectroscopy

$\text{Zn}_{1-x}\text{Sm}_x\text{O (x = 0.01, 0.03 and 0.05)}$ NPs showed a decrease in reflectance in UV-vis spectra which is shown in figure 4a. The light was scattered by grain boundaries of smaller-sized doped NPs which reduces reflectance[19]. Figure 4b illustrates the strong absorption threshold of pristine and doped NPs near 370 nm. The absorption edge widens as doping was increased and shifts to higher energy. Red shift and enhanced visible light absorption ability were observed with increasing concentration due to the narrower band gap. In this case, electron and hole are transferred between 4f orbital of Sm ion and ZnO valence or conduction band[57, 58]. For $\text{Zn}_{0.95}\text{Sm}_{0.05}\text{O}$, absorption in the visible region was slightly decreased as further doping is responsible for surface defects. Kubelka-Munc formula was used for calculating band gaps and are listed in Table 3[59]. $\text{Zn}_{0.97}\text{Sm}_{0.03}\text{O}$ showed least band gap of 3.18 eV which is created by excessive energy surfaces between conduction and valence bands of ZnO compared to others (figure 5)[60]. Due to the Moss-Burstein effect further doping increased the band gap, pointing out that low energy transitions are blocked as with increasing dopant concentration, fermi level within conduction bands moves upward[61, 62]. From the theoretical study discussed later, it is found that band gap decreases on 5 mole percent doping. Though the trend of experimental band gap contradicts with the trend of computational band gap beyond 3 mole percent doping, a similar trend is found when the impurity states were taken into account.

3.4 Photoluminescence Spectroscopy (PL)

Photoluminescence spectra were studied for understanding the defect states and presented in figure 6. Near band emission (NBE) is appeared as a sharp peak in the UV area as a result of excitonic non-radiative recombination[19]. Emission wavelengths were used to calculate band gap which were quite similar to the band gaps measured by the Kubelka-Muck function and is represented in Table 3. Deep level emissions (DLE) were represented by the broad orange peaks near 600 nm[19, 63]. Oxygen interstitial ($O_i^{2-}$) defects were created while doping to maintain charge balance which is represented by:

$$3\text{Zn}^{2+} = 2\text{Sm}_{\text{Zn}}^{3+} + \text{Zn}^{2+} + O_i^{2-}[19, 64].$$

Radiative recombination amid metastable states leads to strong orange luminescence. Photo-generated electron-hole recombination rate was mitigated resulting in decreased orange peak intensity up to 3 mole percent addition[53, 65]. However, as dopant concentration increases beyond 3 mole percent, the recombination rate was increased slightly which was evident from the marginal increase in the peak intensity (figure 6). As defects increase with increasing dopant concentration, they might become a center for recombination in $\text{Zn}_{0.95}\text{Sm}_{0.05}\text{O}$[66]. Defect annihilation or larger particle size (figure 2d) where recombination can take place before charge carriers reach particle surface, can also be responsible for the increased peak intensity[67].

3.5 X-ray Photoelectron Spectroscopy (XPS)

Figure 7a shows survey scans of ZnO and $\text{Zn}_{0.97}\text{Sm}_{0.03}\text{O}$ NPs. The survey scan of ZnO reveals the presence of Zn, O and C. Either CO/CO$_2$ absorption in the surface or air contamination is responsible for C1s peak[66]. Two peaks of Sm are found in the survey scan of $\text{Zn}_{0.97}\text{Sm}_{0.03}\text{O}$. From the high resolution
scan of Zn 2P of ZnO, the difference in binding energy between Zn 2p1/2 (1044.69 eV) and Zn 2P3/2 (1021.64 eV) is found around 23.05 eV which confirms that Zn is present in Zn$^{2+}$ oxidation state (figure 7b)[68]. When Sm is added, this difference changes slightly to around 23.11 eV and both Zn 2p1/2 (1044.45 eV) and Zn 2P3/2 (1021.34 eV) peaks shift to lower binding energies corresponds to the electronic interactions of Sm with the lattice (figure 7b)[68]. Figures 7c and 7d represent the scan of O 1s of ZnO and Zn$_{0.97}$Sm$_{0.03}$O, respectively. From the deconvolution of the O 1s peak, three distinct fitted peaks are observed in both cases. The fitted peaks at around 530.13 eV for ZnO and 529.94 eV for Zn$_{0.97}$Sm$_{0.03}$O represent the presence of lattice Oxygen [69]. The absorbed oxygen on the surface attributes to the peaks at around 531.66 eV and 531.46 eV in ZnO and Zn$_{0.97}$Sm$_{0.03}$O, respectively[66].

The other peak at 533.14 eV in ZnO and 532.40 eV in Zn$_{0.97}$Sm$_{0.03}$O corresponds to the absorbed hydroxyl species from water[69]. It is evident from figure 7e that two peaks of Sm 3d3/2 and Sm 3d5/2 are present at around 1110.27 eV and 1083.29 eV, respectively. These peaks confirm the presence of Sm$^{3+}$ in the lattice structure[70]. The absence of other peaks of Sm further confirms that Sm is only present in the trivalent state and no secondary phase of Sm$_2$O$_3$ is present in the lattice[71].

Table 3
Comparison of band gap calculated in different methods.

| Element                | Calculated Band Gap (eV) | From Kubelka-Muck Function | From PL spectra | From DFT Calculation |
|------------------------|--------------------------|-----------------------------|-----------------|----------------------|
| ZnO                    | 3.25                     | 3.14                        | 3.24            |
| Zn$_{0.99}$Sm$_{0.01}$O| 3.23                     | 3.14                        | 3.19            |
| Zn$_{0.97}$Sm$_{0.03}$O| 3.18                     | 3.12                        | 3.12            |
| Zn$_{0.95}$Sm$_{0.05}$O| 3.22                     | 3.13                        | 3.06            |

3.6 Photocatalytic Degradation Test

ZnO and Zn$_{0.97}$Sm$_{0.03}$O NPs were taken to perform the degradation test of a standard dye, RhB, using the visible light filter. Zn$_{0.97}$Sm$_{0.03}$O NPs are selected as the optimum concentration among doped products as these NPs exhibit a lower recombination rate of photogenerated electron-hole pairs along with the least band gap which is essential for photocatalytic activity[64]. It is evident from figure 8(a, b) that with UV radiation, the absorption peak of RhB dye decreased steadily for both the nanoparticles. After 3 hours’ irradiations under UV-light, 56% and 80% degradation were observed for ZnO and Zn$_{0.97}$Sm$_{0.03}$O, respectively. Figure 8(c) shows superior degradation was found for Zn$_{0.97}$Sm$_{0.03}$O NPs. This is because of the lower recombination rate of photo-generated charge carriers. The particles were smaller which is also favorable for photocatalytic reactions as the surface area to volume ratio is higher for Zn$_{0.97}$Sm$_{0.03}$O than pristine ZnO nanoparticles[32, 58, 64, 72]. The kinetic equation of Langmuir-Hinshelwood (L-H) can be used to model the degradation of several dyes by heterogeneous semiconductors used as photocatalysts[73]. Equation 1 is applicable when the initial concentration is low.
\[
\ln \frac{c_0}{c} = Kt
\]  
(1)

Here, \(c_0\) is the original concentration of organic dye at \(t=0\). The final concentrations at \(t = t\) is \(c\). \(K\) is the apparent first-order rate constant. Pristine and \(\text{Zn}_{0.97}\text{Sm}_{0.03}\text{O}\) nanoparticles showed a linear relationship when \(\ln(c_0/c)\) was plotted against time which is presented in figure 8(d). \(K\) was calculated 0.00435 min\(^{-1}\) and 0.00852 min\(^{-1}\) for pure and \(\text{Zn}_{0.97}\text{Sm}_{0.03}\text{O}\), respectively. 1.95 times higher rate of degradation was found for \(\text{Zn}_{0.97}\text{Sm}_{0.03}\text{O}\) nanoparticles compared to pristine ZnO NPs. Figure 8(e) illustrates the recyclability test of \(\text{Zn}_{0.97}\text{Sm}_{0.03}\text{O}\) nanoparticles under identical test conditions. After four consecutive cycles, degradation efficiency slightly decreased under similar experimental condition. This happens due to the slight loss of nanoparticles during recycling. Figure 8(f) shows a visual representation of the continual discoloration of RhB dye to degradation caused by \(\text{Zn}_{0.97}\text{Sm}_{0.03}\text{O}\) nanoparticles under UV illumination.

\(\text{Sm}^{3+}\) possesses the ability to separate photogenerated electron-hole pairs which is evident by photoluminescence spectra where all the \(\text{Sm}^{3+}\) doped ZnO NPs showed a lower electron-hole recombination rate compared to pristine. Thus, reactive species such as hydroxyl radicals (OH\(^+\)), superoxide anion radicals (O\(_2\)\(^{•−}\)) could be generated when samarium is introduced into the ZnO matrix.\(^{[64, 74]}\) \(\text{Sm}^{3+}\) having partially filled f-elections can mitigate electron-hole recombination by trapping electrons of the conduction band which is produced by irradiation.\(^{[58, 75]}\) Unstable \(\text{Sm}^{2+}\) can easily transfer this electron to produce superoxide anion radical followed by producing hydroxyl radicals in subsequent steps. These active OH\(^+\) radicals react with RhB and decompose it\(^{[36]}\). This mechanism is postulated in figure 9 and the related reactions are listed below:

\[
\text{ZnO} + \text{hv} \rightarrow \text{ZnO} \left(\text{e}^{−}_{(CB)}\right) + \left(\text{h}^{+}_{(VB)}\right)
\]

\[
\text{Sm}^{3+} + \text{e}^{−}_{(CB)} \rightarrow \text{Sm}^{2+} \text{ (Trapping of electron)}
\]

\[
\text{Sm}^{2+} + \text{O}_2^{−} \rightarrow \text{Sm}^{3+} + \text{O}_2^{•−} \text{ (Transfer of electron)}
\]

\[
\text{O}_2^{•−} + \text{H}^{+} \rightarrow \text{OOH}^{•}
\]

\[
\text{OOH}^{•} + \text{H}^{+} + \text{e}^{−}_{(CB)} \rightarrow \text{H}_2\text{O}_2
\]

\[
\text{H}_2\text{O}_2 + \text{e}^{−}_{(CB)} \rightarrow \text{OH}^{•} + \text{OH}^{−}
\]

\[
\text{RhB} + \text{OH}^{•} \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

Furthermore, photogenerated holes could also produce hydroxyl radicals by reacting with water molecules on the surface of the catalysts which may also take part in the degradation process by the following reactions:
\[ h^+_{(VB)} + H_2O \rightarrow H^+ + OH^- \]

\[ h^+_{(VB)} + OH^- \rightarrow OH^- \]

### 3.7 First principle analysis using DFT

For calculating the different properties from DFT for different Sm\(^{3+}\) concentrations in ZnO, supercells have been built having various sizes. 4x4x3, 3x3x2 and 3x3x1 supercells of ZnO are used as models for 1.04, 2.80 and 5.50 mole% Sm\(^{3+}\) doping, respectively and presented in figure 10(a-d). They are the closest doping percentages possible for Sm\(^{3+}\) doping which is comparable to experimental studies viz. for mole percentages 1, 3 and 5. As the atomic radius of dopant and host lattice atoms varied, crystal structures changes differently. Lattice parameters for pure ZnO are calculated by DFT analysis and found to be \(a=b= 3.28 \, \text{Å} \) and \(c=5.30 \, \text{Å}\). When DFT+U approach was employed a slight change in lattice parameter is observed where \(a=b= 3.05 \, \text{Å} \) and \(c= 4.92 \, \text{Å}\). These values are analogous to the experimentally-calculated parameters as well as the parameter calculated by the DFT and DFT+U approach in previous studies of ZnO\([45, 76]\).

The bond length changes greatly near the doping positions as the radius of Sm\(^{3+}\) ion is greater than that of Zn\(^{2+}\) ion, which may be ascribed to the difference of the atomic radius and the number of valence electrons between dopants and the host atoms. The bond lengths of pristine and doped ZnO NPs are listed in Table 4. From the relaxed structure, it is revealed that the crystal structure shows some distortion after doping which is localized only around the impurity atom. The Sm-O bond length increased progressively with increasing doping. Due to this increasing bond length, the lattice constant (c/a) is also increasing with the doping concentrations of Sm\(^{3+}\) which is evident from XRD analysis. As Sm\(^{3+}\) ions turn out to be more closely space out for increasing doping, greater impurity-impurity contact expanded the bond length. This also affects electronic properties.

| Element       | Bond length (Zn-O) near Sm atom | Bond length (Sm-O) |
|---------------|---------------------------------|-------------------|
| ZnO           | 2.001 Å (DFT), 1.87 Å (DFT+U)   | N/A               |
| Zn\(_{0.99}\)Sm\(_{0.01}\)O | 1.87 Å (DFT+U)                  | 2.26 Å (DFT+U)    |
| Zn\(_{0.97}\)Sm\(_{0.03}\)O | 1.87 Å (DFT+U)                  | 2.27 Å (DFT+U)    |
| Zn\(_{0.95}\)Sm\(_{0.05}\)O | 1.88 Å (DFT+U)                  | 2.31 Å (DFT+U)    |

From calculation, a direct bandgap of 0.72 eV is found at \(\Gamma\) point (figure 11a). This is much less significant than the investigational value of 3.25 eV. Often standard DFT underestimates bandgap of ZnO. So effective on-site Coulomb interaction (U) (DFT + U) was used with density functional theory (DFT). Usually, standard Kohn–Sham eigenvalues exclude quasiparticle energies. So, the inadequate
treatment of quasi-core electrons of a deeply correlated structure like ZnO which leads to a strong p-d hybridization. This is a very common issue for many strongly correlated systems.

The value for $U_{\text{eff}}$ as 10.8 eV for zinc d orbital and 7 eV for oxygen p orbital was used. Thus, a direct band gap of 3.25 eV was calculated which is comparable to the value of 3.25 eV, which was found experimentally (figure 11b). But the reduction in the bond length along with lattice parameters was measured. The localization of the d-state reduced the lattice constant which further drags the electron toward the core. For the rest of the calculations, these $U_{\text{eff}}$ values were used.

The spin-polarized DOS and band structure for different doping concentrations of Sm$^{3+}$ were calculated. The calculated projected density of states (PDOS) for the nanoparticles as a function of energy is plotted in figure 12. The valence band of undoped ZnO is created by firmly hybridized 0 2p and Zn 3d orbitals. Here, the impact from 0 2p orbital is greater. From the color gradient in figure 12, it is evident that the conduction band minima (CBM) is composed of orbitals of both Zn and O atoms. There is no atomic magnetization is observed for pure ZnO as evident from the symmetric DOS. Later, magnetization was calculated as zero for this calculation. The upper valence band of doped ZnO from -2.5 eV to approximately -7.5 eV originates primarily from the O 2p and Zn 3d orbitals. As Sm$^{3+}$ has more valence electrons than Zn$^{2+}$, with doping the system becomes more n-type. Here, fermi level moves towards the conduction band for all three doped cases. Interestingly, Sm$^{3+}$ has introduced some impurity states from Sm 4f orbital in the gap region. Sm 4f and 5d orbitals in the conduction band also contribute to a little extent in addition to Zn and O atom orbitals.

Contribution from Sm 4f and 5d orbitals near the conduction band region is visible from the PDOS where the contribution from Sm 5d orbitals is more prominent. So, the Sm 5d and Sm 4f orbitals are responsible for the change in the bandgap. Sm 5d orbitals pushed the conduction band region towards Fermi level. This makes the bandgap smaller as doping concentration increases gradually. Figure 13(a-c) represents the band structure of Sm$^{3+}$ doped ZnO NPs with increasing dopant concentration. From the DFT calculation band gap is calculated as 3.19, 3.12 and 3.06 eV for 1.04, 2.8, and 5.5 mole % doping, respectively. All values correspond to the experimental findings to show the trend of band gap tuning up to 3 mole percentage addition. However, for 5 mole percent doing the trend is different from experimental and DFT results. Consideration of the impurity states caused by doping can explain this difference.

In the case of 1.04% doping, there are some impurity states introduced in the middle of the bandgap region. These impurity states are originated from Sm 4f orbitals. As the concentration of Sm$^{3+}$ increased, more states are introduced in the bandgap region. However, impurity orbitals are found under Fermi level i.e., these states can be occupied by electrons. As a result, these impurity states must have some significant effect on bandgap. If the bandgap is considered from the upper edges of the impurity states to the lower edge of conduction band minima, bandgap change with a similar trend to the experimental results is found. From this calculation 0.67, 0.48 and 0.75 eV bandgap are found for 1.08, 2.8 and 5.5 mole percent doping, respectively. Thus, the minimum band gap was found for 2.8 mol % dopant concentration which follows the findings of experimental results. So, the dopant concentrations i.e.,
Impurity states play a major role in bandgap tuning. These band gap values are quite different than those band gaps obtained experimentally since the defect states are created at a deep level, however, this shows that because of defect states band gap may decrease experimentally for 5 mole percent doping.

For both 1.04 and 5.5 mole percent doping, the localized impurity states were formed very near to Fermi level. The trapped states serve as the recombination centers for charge carriers. But the scenario is different for 2.8 mole % dopant concentration as the impurity states are not that much localized and are well spaced spreading in between the Fermi level and valence band maxima (VBM). These states can act as hole trapping sites that can reduce the carrier recombination rates. This result is shown well agreement with the PL observations and suggests that photocatalytic performance should be best for 3 mole percent doping. However, photocatalytic degradation was investigated only for Zn$_{0.97}$Sm$_{0.03}$O among the doped ZnO considering the fact that PL study showed minimum recombination rate of charge carriers for 3 mole percent doping and no significant change in band gap was observed for further doping beyond this doping concentration.

4 Conclusion

Zn$_{1-x}$Sm$_x$O ($x = 0.01, 0.03$ and $0.05$) NPs were produced by a modified sol-gel route followed by a comprehensive analysis focusing on structural and optical characteristics. No peaks for the extra phase was present in XRD which confirms the complete dissolution of Sm$^{3+}$ into the lattice. Moreover, the presence of trivalent Sm$^{3+}$ in XPS further confirms that there was no secondary phase of Sm$_2$O$_3$. On doping, particles became smaller up to 3 mole percent dopant concentration. It was observed that Sm$^{3+}$ doping effectively enhanced the visible light absorbability of ZnO NPs along with red shift and the least band gap of 3.18 eV was observed for 3 mole percent doping. Moreover, Sm$^{3+}$ doping facilitates radiative recombination of photogenerated holes and electrons and thus produces an orange band in the spectrum. It is evident from PL that the lowest recombination rate was observed for Zn$_{0.97}$Sm$_{0.03}$O NPs which makes it favorable for photocatalytic applications. Zn$_{0.97}$Sm$_{0.03}$O NPs showed 1.95 times greater degradation of RhB dye compared to pristine ZnO NPs because of its low recombination rate and smaller-sized particles with a high surface to volume ratio. Finally, the DFT study showed that calculated band gap values are comparable with experimental findings with a similar trend up to 3 mole percent dopant addition and consideration of the defect states created by doping can predict band gap changing trend for further doping beyond this dopant concentration. DFT study also predicts the lowest recombination rate for Zn$_{0.97}$Sm$_{0.03}$O which agrees well with the results found from PL spectra and suggests the highest photocatalytic performance for this dopant concentration.

Declarations

CONFLICTS OF INTEREST

There are no conflicts of interest to declare.
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**Figures**

**Figure 1**

Reduction in XRD peak intensity with increasing Sm3+ concentration.
Figure 2

FESEM micrographs of (a) undoped, (b) Zn0.99Sm0.01O, (c) Zn0.97Sm0.03O and (d) Zn0.95Sm0.05O NPs showing morphological changes
Figure 3

TEM images of (a), (b) ZnO and (c), (d) Zn0.97Sm0.03O exhibiting reduced particle size on doing.
Figure 4

Curve of (a) reflectance and (b) absorbance variation from UV-vis DRS spectra

Figure 5

Optical band gap variation with increasing doping amount calculated using UV-vis DRS spectra using Kulbelka-Muck function
Figure 6

Photoluminescence spectra exhibiting (a) near band gap emission and (b) orange luminescence.
Figure 7

(a) XPS survey spectra of ZnO and Zn0.97Sm0.03O, (b) High resolution scans of Zn 2P of ZnO and Zn0.97Sm0.03O, (c) High resolution scan with deconvolution of O 1s of ZnO, (d) High resolution scan with deconvolution of O 1s of Zn0.97Sm0.03O and (e) High resolution scan of Sm 3d of Zn0.97Sm0.03O.
Figure 8

(a) absorption spectra of RhB with ZnO suspension, (b) absorption spectra of RhB with Zn0.97Sm0.03O suspension, (c) RhB degradation for blank, pristine and Zn0.97Sm0.03O, (d) degradation rate constant, k, (e) reusability of Zn0.97Sm0.03O for 4 consecutive runs and (f) Visual illustration of RhB degradation in the presence of Zn0.97Sm0.03O.
Figure 9

Proposed Photocatalytic Mechanism of Sm3+ doped ZnO

Figure 10

(a) ZnO unit cell, (b)-(e) 1.04, 2.8 and 5.5 mole percent Sm3+ doped ZnO supercell, respectively. Zn2+ are represents with gray balls, O2- with red balls and Sm3+ with blue balls.
Figure 11

Band structure of pure ZnO using (a) DFT approximation and (b) DFT+U approximation.
Figure 12

Projected density of states for pristine and Sm3+ doped ZnO.
Figure 13

Band structure of (a) 1.04 (b) 2.8 and (c) 5.5 mole percent Sm3+ dopped ZnO.