Sm$^{3+}$ driven enhancement in photocatalytic degradation of hazardous dyes and photoluminescence properties of hexagonal-ZnO nanocolumns

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Abstract

Samarium doped ZnO (Sm-ZnO) nanocolumns were grown by wet chemical method and the doping effect of Sm$^{3+}$ on visible light photocatalytic (PC) and photoluminescence (PL) properties of ZnO was investigated. Methylene blue (MB) and methyl orange (MO) were considered for the degradation study as a step initiated towards the remediation of industrial wastewater. Subsequent characterization studies by x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) enumerate that the hexagonal-wurtzite structured Sm-ZnO is highly crystalline in nature and possesses hexagonal column like nano-architectures. Although, a charge imbalance exists between the ions, the substituional effects of Sm$^{3+}$ at Zn$^{2+}$ sites have been observed from the XRD spectra and discussed by suitable mechanisms. FTIR measurement gives the information on the evolution of peaks related to metal-oxygen bond in Sm-ZnO which may be linked with Sm ions. PC measurement shows that the degradation efficiency of 95% can be achieved by Sm-ZnO photocatalysts in degrading MB and 91% for MO. Sm doping induces high charge separation efficiency and generation of OH ions in ZnO leading to such improvisation in degradation efficiency. The prepared Sm-ZnO nanocatalysts possess high degree of photostability and reusability even after fourth cycle of photodegradation. PL spectra show the suppression of the sharp and intense excitonic emission band of ZnO in Sm-ZnO due to low rated direct recombination of carriers. Incorporation of Sm$^{3+}$ ends up with intrinsic defect mediated enhancement in the visible emissions especially in the blue, yellow and red region of light spectrum.

1. Introduction

ZnO has been evolved as a novel semiconducting material with notable improvement in the structural/optical attributes when its size turns down to nanoscale [1]. Highly desirable products with applications in the field of bio-imaging/drug delivery, solar cell, piezotronic devices, photo-detection and light emitting diodes can be easily achievable with diverse morphologies of nano ZnO [2–7]. Photocatalysis under visible light irradiation is one of the properties demonstrated by ZnO nanoparticles for which these are widely admired in catering the challenges of environment pollution [8–15]. Harmful and hazardous effluents from the industries are treated as water-borne pollutants and can be degraded using nano ZnO as a photocatalyst in an effective manner. ZnO has also attained high visibility in demonstrating novel luminescent properties which are applicable in ultraviolet and lasing devices [16]. This is possible due to features like wide direct band gap (3.37 eV) and high excitonic binding energy (60 meV) with high chemical stability of ZnO which have eventually pushed it into a new height of success in the above fields in comparison to other metal oxides [15, 17–19].

Photocatalysis is a very efficient and desirable method for the degradation of toxic and carcinogenic organic pollutants. These pollutants are found as dyes, detergents, and volatile organic compounds secreted from industries linked with petroleum products, paint, textile, pesticides, printing, and pharmaceuticals [7, 20, 21].
Environment pollution can be reduced by conversion of these pollutants into simpler and harmless compounds in an eco-friendly and inexpensive way. There exists some physico-chemical methods such as; adsorption, coagulation, and ion-exchange which fail to demineralize and remove the pollutants completely from the effluents due to their complex chemical and molecular structure [22]. These conventional methods of treating the wastewater result in the conversion of the pollutants from one form to another which is even more harmful than the initial configuration [23]. So, there is a requirement to adopt versatile methods such as semiconductor based advanced oxidation processes (AOPs) which are proved to be efficacious in the degradation of toxic dyes in aqueous suspensions. This will be a highly beneficial and remedial approach for treating wastewater and catering environment pollution causing due to it. Similarly, luminescence properties of materials are of utmost importance for fabrication of multi-colored LEDs, flat panel displays and phosphor elements with enhanced visible emission [24]. Enhancement of the UV and visible emissions from metal oxide semiconducting nanoparticles for the above applications is evolved as the major thrust areas for material scientists and considered as one of the indispensable research problems.

Doping of key elements is a salient and influential approach for tailoring the photocatalytic and photoluminescence properties of semiconducting ZnO [25, 26]. Incorporation of foreign elements into ZnO will confiscate the main hindrances such as low quantum yields and fast recombination of the photo-generated electron-hole pairs (EHP) hampering the photodegradation efficiency of ZnO [22, 26, 27]. Doping of ZnO, especially with rare earth (RE) ions induces surface defects along with trapping centers in the band gap which result in the inhibition of EHP recombination and acceleration of the interfacial charge transfer [27]. Enhancement in the visible range photoluminescence properties has also been observed in ZnO:Eu, ZnO:Gd, ZnO:Er, ZnO:Yb, ZnO:Ce and ZnO:Sm systems due to the 4f electronic contributions from the RE ions [28, 29]. Sm3+ with five 4f electrons offers a modulation in the energy transfer mechanism from the host ZnO upon mingling in the crystalline matrix [28]. It eventually helps in elevating the visible light photocatalytic performance including visible light emissions in ZnO [23, 30, 31]. Our present investigation is focused in this direction and we have tried to enhance the photocatalytic degradation of methylene blue (MB) and methyl orange (MO) dyes by preparing Sm doped ZnO nano-catalysts. Efforts have also been invested in improvisation of the PL emission properties of ZnO by Sm doping. To the best of our knowledge, a very few reports are available on the above subject with convincing mechanism but no literature is available on the photodegradation study of methyl orange by Sm-ZnO.

2. Materials and method

The chemical reagents were used for the synthesis of Sm-ZnO were of analytical reagent (AR) grade of 99.99% purity purchased from M/s Sigma Aldrich and utilized without further purification. Zinc acetate dihydrate (Zn(CH3COO)2·2H2O) and samarium (III) nitrate hexahydrate (Sm(NO3)3·6H2O) were taken stoichiometrically along with liquid ammonia as pH regulator for preparing the nanocrystallites. 0.2 M zinc acetate dihydrate was taken in 20 ml of deionised water and the experimental procedure was followed as described in our previous report [17]. Following the above process, Sm-ZnO nanoparticles were prepared by taking 0.001 M, 0.002 M and 0.003 M concentrations of samarium nitrate and accordingly the samples were named as ZSM1, ZSM2 and ZSM3 respectively. The samples were dried in an oven at 100 °C overnight with further grinding by a pestle mortar.

Crystal structure and phase analysis of the products were carried out by a diffractometer (X′ Pert Pro, M/s Panalytical) equipped with Cu-Kα radiation (λ = 1.540 Å) and operated at 40 kV and 30 mA. Morphology and chemical composition of the doped sample were analyzed by a field emission scanning electron microscope (Carl Zeiss, SMT AG). A PL spectrophometer (M/s Horiba) with He-CD LASER as the excitation source was deployed to record the spectra. The Fourier transformed infrared (FTIR) spectra (4000–400 cm⁻¹) were recorded by the help of a Perkin Elmer FTIR spectrometer (Spectrum GX).

The photo-degradation study of the samples was carried out under visible light irradiation. During this process, 0.1 g of the prepared catalyst (ZSM3) was added to 50 ml of 10⁻⁴ M methylene blue (MB) solution having original concentration of 5 mg l⁻¹. The mixture of catalyst and MB was stirred continuously with a magnetic stirrer and kept in a quartz photo-reactor in the dark for 60 min to create an adsorption/desorption equilibrium of the dye. The mixture was irradiated with a visible light lamp (20 W) as the light source. Throughout the process, 5 ml of the mixture solution was sampled periodically. The absorbance of the solution at λmax = 664 nm was recorded by using a UV–vis spectrophotometer. Similar experiment was conducted for methyl orange dye at λmax = 464 nm and the photo-degradation study was performed on regular interval of time. The degradation kinetics was studied by plotting ln(C0/Co) with respect to irradiation time [18]. The degradation efficiency was calculated by the following equation for both MB and MO.
Degradation efficiency \( \frac{[(C_0 - C_t) / C_0] \times 100}{= \text{Degradation efficiency}} \)

Here, \( C_0 \) and \( C_t \) are the concentration before and after treatment with visible light.

3. Result and discussion

3.1. Structural and morphological analysis

The nature of the samples including phase study and crystallographic orientation has been investigated by powder x-ray diffraction method and the spectra of pure ZnO along with Sm-ZnO have been depicted in figure 1(a). The XRD patterns of all the samples show the formation of hexagonal wurtzite structured ZnO with \( P6_3 \text{mc} \) as space group. The crystallinity of the samples is very high and evolution of no secondary phases is not observed. This may be due to the uniform substitution of Sm\(^{3+} \) ions at the Zn\(^{2+} \) sites resulting no subsidiary phases [26]. The XRD peaks of Sm-ZnO are observed to be broader and weaker in intensity as compared to ZnO inferring the inhibition of ZnO growth with incorporation of samarium ions. The crystallite size of the samples have been calculated and found to be 28 nm, 28 nm, 26 nm and 25 nm for ZnO and Sm-ZnO (0.001 M, 0.002 M & 0.003 M) respectively. The crystallite size of Sm-ZnO decreases as compared to pristine ZnO. This decrease may be attributed to the generation of Sm-O-Zn bonds inhibiting nucleation and ZnO crystal growth [22].

Other rare earth ions also demonstrate similar effects when doped into ZnO [23]. The shifting of diffraction peaks of the doped samples towards lower angle side in the 30°–38° range of 2\( \theta \) has been observed and illustrated in figure 1(b). This symbolizes the effect of Sm doping and its substitution at the Zn sites [28, 29, 32]. There exists a difference in the ionic radii of Zn\(^{2+} \) (0.074 nm) and Sm\(^{3+} \) (0.096 nm). So, the charge imbalance is the major issue which needs to be addressed for successful doping of elements like rare earth ions into ZnO [33, 34]. This charge imbalance can be intentionally compensated by adopting a well-designed synthesis mechanism [35]. Suitable monovalent cations are also introduced as charge compensators during the process of synthesis to cater the above challenge [35, 36]. In this case, two Zn\(^{2+} \) ions are replaced by one Sm\(^{3+} \) ion and the above monovalent cation (MC\(^{+} \)) as given below [36].

\[
2\text{Zn}^{2+} \rightarrow \text{Sm}^{3+} + \text{MC}^{+}
\]

There exist two other possible mechanisms to maintain the charge neutrality by the generation of crystal defects in the absence of monovalent charge compensator ion. In the first case, the charge compensation is carried out by a zinc vacancy (\( V_{\text{Zn}} \)) defect where three Zn\(^{2+} \) ions are replaced by two Sm\(^{3+} \) ions along with a \( V_{\text{Zn}} \) defect (3Zn\(^{2+} \) \rightarrow 2Sm\(^{3+} \) + \( V_{\text{Zn}} \)) [36]. In the second case, one oxygen interstitial defect is created upon the replacement of two Zn\(^{2+} \) ions by two Sm\(^{3+} \) ions (2Zn\(^{2+} \) \rightarrow 2Sm\(^{3+} \) + O\(^{2-} \)) [36]. In our case, the evolution of crystal defects leads to the deformation of ZnO lattice upon substitution of samarium ions and results such peak shift [25]. These effects will also contribute to a change in the inter-planar spacing and lattice micro-strain (MS). MS has been calculated and found to increase upon Sm doping. The values of crystallite size and strain have been provided in table 1.
Morphology of Sm-ZnO (ZSM3) sample has been studied by an electron microscope and the micrographs have been illustrated in figure 2. It shows the formation of hexagonal nanocolumns of ZnO uniformly distributed throughout the surface. The length of the nanocolumns varies from 400 nm to 800 nm. Nucleation and growth of these nanocolumns from a single point leading to hybrid structures are also observed. A high resolution image (figure 2(b)) shows the existence of a hexagonal top surface of the nanocolumns having dimension of one side varying from 40 to 70 nm. Chemical composition of the sample has also been studied by EDAX measurements and the spectrograph is shown in figure 2(b) as an inset. This confirms the existence of Sm ions in ZnO lattice.

### Table 1. Crystallographic parameters of ZnO and Sm-ZnO nanocrystallites.

| Name of Sample | Crystallite size (nm) | Micro-strain |
|----------------|-----------------------|--------------|
| ZnO            | 28                    | 0.003        |
| ZSM1           | 28                    | 0.006        |
| ZSM2           | 26                    | 0.011        |
| ZSM3           | 25                    | 0.015        |

3.2. FTIR study

FTIR spectra of pristine ZnO and Sm-doped ZnO nanoparticles have been illustrated in figure 3. The pattern of ZnO shows an intense sharp band at 432 cm\(^{-1}\) which is attributed to E\(^{2\text{high}}\) (ZnO non-polar optical phonon) mode [37]. This is the characteristic peak of wurtzite ZnO [38]. But, for the Sm-ZnO samples, a new band at 465 cm\(^{-1}\) appears which may be ascribed to Sm-O bonds. Generally, the signature of metal-oxygen bond is observed in the region of 400–700 cm\(^{-1}\) [18]. The broad band between 3400 and 3700 cm\(^{-1}\) belongs to the stretching vibrations of hydrogen-bonded surface water molecules and hydroxyl groups [39]. The prepared samples may rapidly adsorb water from the atmosphere due to high surface area shown in FESEM images. The bands appearing in the region 1435–1650 cm\(^{-1}\) may be due to the bending vibration of coordinated water [39]. There exists two other bands at 1355 and 1520 cm\(^{-1}\) which originate mainly due to COO– modes from the carboxyl groups of zinc acetate as precursors with symmetric and asymmetric stretching vibrations [40].

3.3. Photocatalytic study

The photocatalytic (PC) degradation study of MO and MB dyes at different time intervals by the application of Sm-ZnO nanoparticles was carried out and the spectra have been depicted in figures 4(a) & (b). The degradation study was performed by quantitative change of concentration and physical change of absorption spectra as a function of wavelength at regular time intervals of 30 min. It has been observed that the photocatalytic activity of Sm doped ZnO shows improved degradation efficiency indicating the effect of Sm doping [41]. The absorption peak of MB dye is observed at 664 nm whose intensity got reduced gradually under the effect of visible light. Similarly, the maximum in the absorption spectrum for MO is observed at 464 nm which loses its intensity with the exposure of visible light in presence of the photocatalyst. The intensity of the absorption peak also decreases with the increase in irradiation time (0–180 min) due to variation in number of photo-generated charge carriers which may be generated during the irradiation of light on the photocatalyst. The variation in

Figure 2. FESEM images of Sm-ZnO nanocolumns with EDAX spectrum (inset) confirming Sm doping.
degradation (%) with irradiation time has been plotted and illustrated in figure 5(a) for MO and MB dyes. The maximum value of degradation efficiency is found to be 94.75% and 90.89% for MB and MO respectively by using Sm-ZnO (ZSM3) photocatalyst under visible light irradiation. We have previously reported the PC performance of undoped ZnO nanocatalyst in degrading MB which was found to be 89% but in the present case, the efficiency is considerably higher [42]. Recently, Sukriti et al. studied the visible-light PC performance of Sm-ZnO to degrade MB dye and achieved a degradation percentage of 94.94% in 60 min [26]. But, the amount of photocatalyst taken for this experiment was 2 g l\(^{-1}\) which is just 5 mg l\(^{-1}\) in our case. Similar experiment was carried out by Hassanzadeh-Tabrizi et al. to study the photodegradation property of ZnO-Ag-Sm system towards MB degradation and found it to be 94% [43]. Abu-Dief et al. studied the wastewater remediation property of Gd\(_2\)O\(_3\)-CdO nanocomposites [44]. The above composite was found to be superior in degrading MB with a photodegradation efficiency of 89.1% which is 44% for pure CdO catalysts. The degradation efficiency of MO was 77.88% for ZnO as reported in our previous report and 90% for Eu-ZnO with same amount of photocatalyst.
Any other report on the photodegradation property of MO by Sm-ZnO is not available in literature. So, our present study gives comparatively better results in line with the existing ones.

The rate of photo-degradation of dyes used in our experiment such as MB and MO follows pseudo first-order kinetics. This has been stated by Langmuir-Hinshel Model which can be observed from figure 5(b) [41]. The degradation kinetics of MB has been studied by A. M. Abu-Dief and W. S. Mohamed group following the above model [45, 46]. Different kinetic parameters such as the rate constant \( (k) \) and the correlation coefficient \( (R) \) have been calculated using the data obtained from the above graph. The rate constant was found to be 0.0323 min\(^{-1}\) and 0.0261 min\(^{-1}\) for MB and MO respectively with \( R \) value of 0.8923. During the photocatalytic experiments, solution of the catalyst was irradiated with visible light to generate electrons and holes in conduction and valence band of ZnO respectively [47–50]. When visible light falls on the catalytic surface, the electrons \( (e_{\text{CB}}^-) \) acquire the excitation energy to jump from the valence band \( (VB) \) to the conduction band \( (CB) \) of semiconducting ZnO by the creation of \( h^+_{\text{VB}} \). The generation of electrons and holes are responsible for the photocatalytic degradation. But, for effective photodegradation process, the recombination rate of the electrons and holes should be slow. So, Sm\(^{3+}\) doping makes ZnO as strong Lewis acid due to the presence of partially filled f-orbitals which can effectively trap the \( (e_{\text{CB}}^-) \) and inhibit the recombination with \( h^+_{\text{VB}} \) [26, 27]. Here, Sm\(^{3+}\) ions can act as electron scavengers and suppress the recombination rate of electron-hole pair. The reduced state of Sm\(^{2+}\) ions, with 6f electrons, is very instable which leads to de-trapping of the conduction band electrons \( (e_{\text{CB}}^-) \) and transfers to the \( O_2 \) molecules encouraging the \( O_2^- \) formation which is finally converted to active \( \cdot\text{OH} \) radicals. So, doping of Sm ions is considered as an effective charge carrier trap which facilitates the movement of excited \( e_{\text{CB}}^- \) during photocatalysis. The degradation mechanism for the Sm-ZnO can be given as [51, 52].

\[
\begin{align*}
\text{ZnO} + h\nu (\text{photons}) & \rightarrow \text{ZnO}(e_{\text{CB}}^- + h^+_{\text{VB}}) \\
\text{Sm}^{3+} + e_{\text{CB}}^- & \rightarrow \text{Sm}^{2+} \\
\text{Sm}^{2+} (\text{unstable}) + O_2 & \rightarrow \text{Sm}^{3+} + O_2^- \\
O_2^- + H^+ & \rightarrow \cdot\text{OOH} \\
\cdot\text{OOH} + H^+ + e_{\text{CB}}^- & \rightarrow H_2O_2 \\
H_2O_2 + e_{\text{CB}}^- & \rightarrow \cdot\text{OH} + OH^- 
\end{align*}
\]

The reactive \( h^+_{\text{VB}} \) present at the valence band can undergo the charge transfer process to generate active \( \cdot\text{OH} \) radicals by getting trapped on the catalyst surface. This charge transfer may takes place with surface-bound hydroxide species or adsorbed water molecules. At the same time, the photo-generated charge carriers can be easily separated for the production of more active \( \cdot\text{OH} \). This may be the effective reason behind the enhancement of the photocatalytic activity.

\[
\begin{align*}
h^+_{\text{VB}} + H_2O & \rightarrow H^+ + \cdot\text{OH} \\
h^+_{\text{VB}} + OH^- & \rightarrow \cdot\text{OH} \\
\text{Dye (MB or MO)} + \cdot\text{OH} & \rightarrow CO_2 + H_2O \text{ (mineralization of dye)}
\end{align*}
\]

The oxidation potential of \( \cdot\text{OH} \) is considered to be high (2.8 to 1.54 eV). This means that it is a highly reactive radical and very useful for the decomposition of organic pollutants into safe byproducts [53]. These hydroxyl radicals are formed by trapping of electrons and holes by oxygen and water molecules acting as scavengers. The hydroxyl radicals react with the molecule of the dye to form degradable products by the process of
mineralization. Here, the photocatalytic efficiency has been enhanced by choosing appropriate amount of dopant, i.e., Sm$^{3+}$ in ZnO which helps in delaying the recombination rate of charge carriers.

The efficiency of the Sm–ZnO catalyst (ZSM3) was studied by conducting the stability test for different cycles of photocatalytic degradation of MO and MB dyes. This will determine the stability and reusability of the catalysts for their long-term performance for environmental applicability [44]. Figures 6(a) & (b) shows the repetitive photocatalytic degradation efficiency for MO and MB dyes as a function of UV exposure time respectively. After each photocatalytic cycle of 180 min, the MO/MB solution was washed several times with distilled water and subjected to centrifugation to isolate the raw Sm–ZnO catalyst. The isolated powder was dried in an oven for further use. It is evident from the figure that after four cycles, the Sm–ZnO photocatalyst experiences a negligible reduction in its degradation efficiency. The minimal reduction in degradation efficiency is may be due to the unavoidable loss of photocatalysts during the cyclic process. This indicates the higher degree of photostability and reusability of the catalyst for different environmental applications.

3.4. Photoluminescence studies

Defect states present in the band gap of ZnO leading to different emissions can be analyzed by investigating the photoluminescence (PL) spectra [6]. Figure 7 depicts the PL emission spectra of pristine ZnO and Sm–ZnO nanoparticles. The samples were irradiated with light corresponding to a wavelength of 325 nm and the emission spectra were recorded. To ascertain the peak positions in the PL spectrum, it has been deconvoluted (assuming the peaks to be Gaussian) and the deconvoluted PL spectra of ZnO and ZSM3 have been illustrated in figure 8. The spectrum of pristine ZnO sample shows one sharp and intense UV emission peak which has been
deconvoluted to give two emission bands at 392 nm and 404 nm. Three other bands appear at 499 nm, 537 nm and 627 nm in the visible region of light spectrum. The UV emission peak is attributed to the near band edge emission in ZnO and represents the recombination of free excitons [17]. The two bands originating after deconvoluting this excitonic emission peak have been assigned to the first and second order phonon replicas of a free exciton band in hexagonal wurtzite structure [54]. Biroju et al observed a similar doublet in the UV region of PL emission spectrum of ZnO and attributed the second small peak in this region originating due the surface states in ZnO [55]. The visible emissions in ZnO originate mainly due to the deep level defect states. The existence of intrinsic defect states such as vacancies and interstitials along with surface defects contributes to the occurrence of visible emissions [28]. In the present case, undoped ZnO shows two green emission bands at 500 nm and 537 nm apart from the excitonic emission. The origin of green emission bands in the region 500–550 nm is described on the basis of the transitions triggered by defect states such as oxygen vacancies (V_O) and oxygen antisites (O_Zn). The radiative recombination taking place between photo-generated holes with the electrons present in the singly ionized oxygen vacancy (V_O^−) state is a major source of this emission process [56, 57]. It has been reported that the V_O^− level lies at 2.48 eV above the valence band (VB) propelling the emission peak to evolve at 500 nm in ZnO [58]. The electrons from the conduction band (CB) jumps to the O_Zn level leading to an emission centered at 537 nm in the green region [59]. The red emission band at 627 nm (1.98 eV) has been ascribed to the transition of electrons from the zinc interstitial level (Zn_i) level to V_p level lying 1.6 eV below the CB [59].

Incorporation of samarium leads to a major transformation in the PL emission spectra of ZnO. The UV excitonic peaks for Sm-ZnO (ZSM3) are found to be blue shifted (384 nm and 393 nm) with samarium doping indicating the expansion of band gap of ZnO [23]. Sm^{3+} acts as a donor in ZnO and results a Moss-Burstein shift of the energy bands showing this broadening [60, 61]. Apart from that, a sharp drop in the intensity of UV emission and rise in the intensity of visible emission is also observed with Sm doping. Suppression of near band edge emission intends the low rated radiative recombination of band edge electron-hole pairs from CB minima to VB maxima achieved by Sm doping. The electrons from the CB may move to different shallow donor levels (Zn_i,−0.22 eV below CB, Sm^{3+}−0.01 eV below CB) acting as electron trapping centers [60]. These electrons may undergo radiative recombination to the holes trapped in different acceptor levels (O_j−2.28 eV below CB and V_{Zn}−3.06 eV below CB) created in the process of substitution of Sm^{3+} at Zn^{2+} sites maintaining charge neutrality [36, 60]. The above process may be one of the major restrictive factors limiting the direct recombination of CB electrons and VB holes and leads to the suppression of near band edge emission. This may ensure a better separation efficiency of photo-generated charge carriers which is highly beneficial for the enhancement of the photocatalytic activity [23]. This has been observed in the present study as discussed in the previous section. The visible emission peaks in ZnO are also substantially altered after Sm doping and has been appeared at 430 nm, 516 nm, 576 nm and 642 nm. The complete new emission band in the blue region at 430 nm (2.88 eV) may be arising due to the transition from Zn_i level to V_{Zn} defect centers originated after Sm doping [62, 63]. The band at 516 nm is linked with the oxygen vacancies as discussed earlier [58]. Two more new bands observed at 576 nm and 642 are ascribed to the ^3H_g2 and ^1H_g2 transitions which are the characteristic emissions of Sm^{3+} [64]. There also exist some other possible mechanisms linked with O_j and V_p defect centers to ascertain the yellow and red emissions in ZnO which may be equally feasible in the present case as we have not observed clear and distinct peaks related to the above characteristic emissions of Sm^{3+} [65]. So, samarium doping induces defect mediated enhanced visible emissions in blue, yellow and red regions for possible applications in optoelectronics.

**Figure 8.** Deconvolution of PL emission spectra of (a) ZnO and (b) ZSM3 nanocrystals.
4. Conclusion

In this study, the action of samarium doped ZnO nanocatalysts on the photodegradation properties of organic dyes like methyl orange and methylene blue have been studied and described. The nanocrystals in the form of hexagonal nanocolumns have been synthesized by wet chemical method and the study of crystallinity by XRD reveals that the materials are in nanocrystalline form. Sm doping induces shrinking of crystal lattice owing to the formation of Zn-Sm-Zn bonds. Hexagonal nanocolumn like morphology has been observed from FESEM studies with EDAX giving the information on impurity doping into ZnO. FTIR study gives the fingerprint of metal-oxygen bond in the spectra. Photocatalytic studies show that Sm-ZnO is very effective in degrading MB and MO dyes and the possible mechanism has been discussed. The degradation efficiency is found to be 95% and 91% for MB and MO respectively under visible light irradiation. The carrier recombination rate in ZnO is significantly delayed by impurity ions (Sm$^{3+}$) leading to such photo-degradation which has also been confirmed from PL studies. Properties like photoactivity and reusability of the SM-ZnO nanocatalysts have been studied and found to be higher for different environmental applications. PL spectra of Sm-ZnO show the suppression of UV excitonic emission band with enhancement in the defect emissions in ZnO. Substitution of Sm$^{3+}$ at Zr$^{4+}$ sites leads to the formation of defect centers like $V_{Zn}$, $O_{l}$ along with intrinsic defects like $Zn_{l}$ and $V_{O}$ which act as acceptor/donor levels in the band gap of ZnO tuning the optical emissions in blue, yellow and red regions.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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