Effect of Doping Rare-Earth Element on the Structural, Morphological, Optical and Photocatalytic Properties of ZnO Nanoparticles in the Degradation of Methylene Blue Dye

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Abstract. ZnO has been widely explored as a remarkable photocatalyst for the degradation of wide ranges of organic pollutants. However, its photocatalytic activity could be enhanced through metal doping. In this study, a rare-earth element, Cerium was doped into the microstructure of ZnO nanoparticles (NPs) using deposition precipitation method to enhance its photocatalytic activity towards methylene blue degradation via UV light irradiation. The resulting degradation efficiencies (DEs) recorded in this study are ~ 64 %, 85 % and 55 % respectively. Similarly, the recorded rates are also found to be 9 x 10⁻³, 21 x10⁻³ and 6 x 10⁻³ respectively, which are well correlated with the DE values. This superior photocatalytic performance achieved by 1 % Ce doping could be attributed to the reduction in band gap of the pure ZnO NPs from 2.69 eV – 2.60 eV. Therefore, 1 % Ce was the optimum doping of Ce⁴⁺ ion into ZnO microstructure, which demonstrates that Ce⁴⁺ ion could be used as an effective tool for stabilizing the generation of the reactive oxygen species, slowing down the recombination of the photo-generated charge carriers as well as enhancing their separation. Therefore, the optimum Ce doping into the ZnO NPs could play a remarkable role in facilitating the structural, microstructural, optical and electronic properties of the ZnO semiconductor, and eventually enhanced its photocatalytic activity.

1. Introduction
Metal oxide nanoparticles (NPs) such as TiO₂, CeO₂ and ZnO have been widely explored as efficient photocatalysts for the degradation of organic pollutants as well as treatment of water and waste water due to their remarkable optical, structural, morphological and electronic properties [1, 2]. ZnO in particular has been widely explored as suitable photocatalyst for the degradation of organic pollutants after TiO₂ due to its simplicity of fabrication and the susceptibility to be moulded into different morphologies while utilizing different methods of synthesis such as hydrothermal, precipitation, sol-gel and vapor deposition among others [3]. Such tendency for the ZnO crystals to be transformed into different sizes and morphologies has been found to be influenced by some reaction conditions such as pH and annealing temperature [4, 5]. Its applications irrespective of the methods of synthesis covers a number of disciplines including gas sensor, dye sensitized solar cells and photocatalysis [6-8]. These applications were influenced by the crystallinity, surface area, presence of defects such as oxygen...
vacancy and zinc interstitials [7, 9]. Among the aforementioned applications, the utilization of ZnO NPs in photocatalysis was found to be remarkable due to its high tendency to absorb visible and ultraviolet radiation, which could subsequently, promotes its optical and electronic properties. The photocatalytic property of the ZnO material towards a number of organic pollutants such as: Methylene blue, rhodamin B dye and direct red-23 dye have been successfully documented in literatures [8, 10, 11]. However, the photocatalytic activity of the ZnO material has been found to be relatively low due to its possession of wide band gap (3.37 eV), low surface area as well as fast electron-hole pair recombination [12, 13]. Several literatures reported the feasibility of enhancing the photocatalytic activity of ZnO material through rare earth metal doping. Rare-earth elements such as Dy, Er, La, Tb, Eu and Nd has been found to enhance the photocatalytic activity of ZnO NPs due to their remarkable light absorption properties, high electrical and thermal conductivity and high Lewis acidity [14-19]. Doping a rare earth elements into the ZnO microstructure could virtually results to either displacement of some of the lattice Zn atoms in the ZnO crystal lattice or probably be dispersed at its surface thereby promoting efficient light absorption and eventually changes the optical, electronic and photocatalytic properties of the ZnO material [18, 20]. In this study, a rare-earth element (Ce) was chosen as the potential dopant into the microstructure of ZnO due to its possession of a stable (+4) oxidation state in addition to the possession of oxidation state of (+3), which is very much common among the rare-earth elements. Its oxide was also found to demonstrate remarkable physical and chemical properties such as high electrical and thermal conductivity and stability, wide surface area and energy band gap, high oxygen mobility and ability to form surface defects such as Ce$^{4+}$ ion and oxygen vacancies [21, 22]. The pure and the Ce doped ZnO NPs were synthesized using precipitation and deposition precipitation methods respectively. The as-calcined samples were subsequently utilized in the photocatalytic degradation of MB dye. MB Dye was used as the model organic pollutant due to its ubiquitous nature and staining properties.

2. Methodology

2.1. Synthesis of undoped ZnO NPs by precipitation and Ce doped ZnO NPs by deposition precipitation

Materials used were analytically graded and they include; Zinc chloride [ZnCl$_2$, MW$= 136.286$ g/mol, Ce(NO$_3$)$_3$.6H$_2$O, MW $= 434.218$ g/mol; Merck Chemicals Ltd], Ammonia solution [NH$_3$.OH, MW$= 35.04$ g/mol, HMBG] and de-ionized water [H$_2$O, MW$= 18.02$g/mol].

The synthesis method utilized in the present study was similar to that employed by Zhang et al. [23]. The ZnO NPs was synthesized using conventional precipitation method. Precisely 1.50g of ZnCl$_2$ was dissolved in 20 ml of distilled water in a 100 ml beaker to form 0.55 M clear homogeneous solution. Upon magnetic stirring at RT, 0.5 ml of NH$_3$.OH was added drop-wise to form cloudy precipitate and the reaction mixture was allowed to proceed for 24 h at 70°C. The resulting cloudy suspension was vacuum filtered, dried at room temperature (RT) and subsequently calcined in air furnace at 400°C for 2 h. The recorded pH of the suspension was 6.3. The as-calcined powder is designated undoped ZnO NPs. The Ce doped ZnO catalysts were synthesized using deposition precipitation method. In this experiment, precisely 0.50 g each of ZnO support catalyst was introduced into a specific amount of Ce (NO$_3$)$_3$.6H$_2$O containing 20 ml of deionized H$_2$O and 0.5 ml of NH$_3$.OH was added drop-wise to form cloudy precipitates. The reactions proceed with a pH of about 11 at all dopant concentrations. The corresponding suspensions were also filtered, dried at RT and subsequently calcined in air furnace at 400°C for 2 h. The calcined powders for the supported catalysts were designated 1 Ce/ZnO and 3 Ce/ZnO corresponding to; 1 wt % Ce doped ZnO NPs and 3 wt % Ce doped ZnO NPs respectively.

2.2. Experimental procedure for the photocatalytic degradation of methylene blue

The photocatalytic reactions were carried out in a transparent spherical glass reactor with 100 ml capacity. Precisely 20 mg each of either ZnO or Ce doped ZnO NPs was mixed with 100 ml of 10-ppm MB solution. The recorded pH of the solution is about 6. Exactly 100 ml of the above mixture was poured into a 100 ml transparent glass spherical reactor and subsequently irradiated with 365 nm UV light in a dark environment. During the period of irradiation, the reaction mixture was continuously
stirred at RT and the mixture was irradiated at different irradiation times between 5 - 100 minutes. About 5 ml of the photo-irradiation mixture was taken at regular intervals (5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100 min), until the final irradiation time of 100 min was achieved. After the irradiation, the mixtures were centrifuged at 3000 rpm for 15 min to obtain the clean samples. The supernatants were collected by means of decantation process and subjected to absorption spectrum measurements using UV-visible spectrophotometer (Shimadzu UV-1601PC, Japan). The schematic of the MB degradation experiment is illustrated in Fig. 1. In order to evaluate the photocatalytic activity as well as the degree of the MB mineralization of the NPs, the following calculation based on degradation efficiency (DE) has been employed [24].

\[
DE (\%) = \frac{A_0 - A}{A_0} \times 100
\]  

(1)

Where DE stands for degradation efficiency in percent, \(A_0\) stands for the MB absorption before UV light irradiation and A is the MB absorption after UV light irradiation of the reaction mixture as a function of irradiation time.

![Figure 1. Schematic illustration of the MB photocatalytic degradation experiment for the Cr/ZnO NPs](image)

2.3. Nanoparticles characterizations
The X-ray diffractions were carried out with a Shimadzu X-ray diffractometer XRD - 7000 using Cu Ka radiation (\(\lambda = 1.54060 \text{ Å}\)) to investigate the structural properties of the undoped and Ce doped ZnO NPs. The ramping rate was set at 5°/min and the X-ray irradiation occurred at 2θ range between 20° to 80°. The field emission scanning electron microscope (FE-SEM) coupled with the energy dispersive X-ray spectroscopy (EDX) (Model; JSM-7610F) were employed to determine the morphology, the average particle size as well as the chemical compositions of the as-calcined samples. The ultraviolet-visible light absorption spectroscopy was used to measure the absorption of the NPs using Cary 500 UV-VIS-NIR Spectrophotometer at RT across 200 nm to 800 nm wavelength range.

3. Results and discussion

3.1. XRD analysis
XRD measurements were carried out on the as-calcined samples to investigate their structural properties. Fig 2. Presents the XRD patterns of the undoped ZnO, 1 Ce/ZnO, and 3 Ce/ZnO NPs. The XRD patterns show strong peaks at various reflections corresponding to the following 2θ values (100, 002, 101, 102, 110, 103, and 112). These reflections are assigned to the crystalline hexagonal wurtzite structure of ZnO material and are also indexed to the JCPDS card no. 89-0510 [25]. The formation of strong peaks confirm the formation of highly crystalline particles. It could be observed that peak intensity increases progressively with Ce doping, indicating that the ZnO crystallinity has improved. The complete absence of any secondary phase in the XRD patterns implies that the hexagonal wurtzite structure of ZnO material is maintained. The complete absence of peaks due to CeO\(_2\) may be attributed to the presence of low amount of doped Ce precursor in the ZnO lattice crystal [5]. Lattice shift was not
observed, indicating that the Ce atom was dispersed across the surface of the ZnO host material rather than substituting the Zn atoms present in the ZnO lattice [26]. This could be attributed to the presence of higher ionic radius of Ce ion, Ce$^{4+}$/Ce$^{3+}$ (0.97 Å/1.03 Å) compared to that of Zn$^{2+}$ ion (0.74 Å) [27].

Similar result was obtained when Eu was doped into the microstructure of ZnO support material [26]. It was also highlighted that the Eu was located at the amorphous or low symmetry site of the ZnO host lattice rather than substituting the Zn atoms of the ZnO crystal lattice [26]. It is also interesting to note that both the undoped and the Ce doped ZnO structural parameters evaluated in this study were estimated by utilizing the XRD data based on the first 3 reflections (100, 002 and 101). The average crystallite sizes for the undoped and the Ce doped ZnO samples were calculated using the known Scherra equation [28].

\[
D = \frac{\kappa \lambda}{FWHM \cos \theta}
\]  

(2)

Where D is the average crystallite size, \( \kappa \) is the dimensionless constant value (0.9), \( \lambda \) is the wavelength of the irradiation and FWHM is the full width at half maximum measured in radian. The calculated average crystallite sizes recorded for the undoped, 1 Ce/ZnO and 3 Ce/ZnO NPs were 31, 51 and 59 nm respectively. These values were presented in Table 1. It is obvious that Ce doping results in the significant increase in the average crystallite size. Similar result was also obtained from literature through doping Tb into the lattice structure of ZnO NPs, with the net effect leading to the increase in the crystallite size and strain of the ZnO NPs.

The lattice parameters (a and c) were calculated using the following equations [29].

\[
\frac{1}{d^2} = \frac{4}{3} \frac{(h^2+k^2+hk)}{a^2} + \frac{l^2}{c^2}
\]  

(3)

Where \( d \) stands for the inter planar spacing, and hkl stands for the miller indices. The values of the lattice parameters were also presented in Table 1. The volume, \( V \) of the unit cell of the hexagonal wurtzite structure of the ZnO was calculated using the following equation [29]:

\[
V = \frac{\sqrt{3}}{2} a^2 c
\]  

(4)

The calculated \( V \) values for the undoped and Ce doped ZnO samples are also presented in Table 1. The position parameter ‘u’ and the Zn-O bond length (L) for the undoped and Ce doped ZnO samples were calculated using the following the equations;

\[
u = \frac{a^2}{3c^2}
\]  

(5)

\[
L = \left[ \frac{1}{3} + \left( \frac{1}{2} - u \right)c^2 \right]^{1/2}
\]  

(6)
The calculated values for both \( u \) and \( L \) are also presented in Table 1. The values of the lattice parameters, \( u \), \( V \) and \( L \) were found to be relatively similar upon Ce doping as shown in Table 1, thus, suggesting the absence of Zn atoms substitution by the Ce atoms in the ZnO host lattice. The specific surface area (\( S_s \)) of the samples were also calculated using the known BET equation [22].

\[
S_s = \frac{6}{D_t \cdot D_{XRD}}
\]  

(7)

The resulting specific surface area values for the undoped ZnO, 1 Ce/ZnO and 3 Ce/ZnO NPs were found to be 35, 21, and 18 m\(^2\)/g respectively as shown in Table 1. Such decrease in the specific surface area of the ZnO NPs upon Ce doping is attributed to the increase in the average crystallite size.

Table 1. The average crystallite size (\( D \)), lattice parameters, LPs (\( a \) and \( c \)), \( u \) parameter, unit cell volume (\( V \)), Zn-O bond length, and specific surface area (\( S_s \)) for the undoped and Ce doped ZnO NPs.

| Material  | \( D \) (nm) | LPs \( a(\text{Å}) \) | LPs \( c(\text{Å}) \) | \( V(\text{Å}^3) \) | \( u \) | \( L(\text{Å}) \) | \( S_s \) |
|-----------|-------------|----------------|----------------|----------------|---|----------|------|
| ZnO       | 31          | 3.255          | 5.196          | 47.675         | 0.131 | 3.673    | 35   |
| 1 %Ce     | 51          | 3.247          | 5.206          | 47.532         | 0.130 | 3.680    | 21   |
| 3 %Ce     | 59          | 3.244          | 5.196          | 47.355         | 0.130 | 3.674    | 18   |

3.2. FE-SEM analysis for the undoped, 1Ce/ZnO and 3 Ce/ZnO NPs

Figure 3. FE-SEM images for the (A) undoped ZnO (B) 1 Ce/ZnO (C) 3 Ce/ZnO and the diameter distribution of (D) undoped ZnO (E) 1 Ce/ZnO (F) 3 Ce/ZnO.
FE-SEM analysis was carried out on the prepared films to determine the particles morphology of the undoped and the Ce doped ZnO NPs. The FE-SEM images for all the analyzed samples are depicted in Fig. 3 (A-C). The same scales (100 nm) and different magnifications (50,000 – 100, 000) were used during the analysis until optimum imaging resolutions were achieved for all samples. It could be clearly seen that all the FE-SEM images show a spherical morphology and wide distributions of different sizes as shown in Fig. 3 (A-C). The recorded ranges of the particle sizes captured are 43.5 – 52.5, 29.1 – 31.2, and 43.8 – 65.3 corresponding to the undoped ZnO, 1 Ce/ZnO, and 3 Ce/ZnO NPs respectively as shown in Fig. 3 (A-C). The Gaussian fitted curves for the undoped and Ce doped ZnO samples were depicted in Fig. 3 (D-F). The estimated average particle sizes were found to be 35.44, 36.64 and 49.22 nm recorded for the undoped ZnO, 1 Ce/ZnO and 3 Ce/ZnO NPs respectively. Results of the average particle size show that the estimated average particle size recorded for the undoped ZnO NPs increases with Ce doping. This trend agreed with the average crystallite sizes calculated using the XRD data as presented in Table 1. The decrease in both the average crystallite and particle sizes of the NPs could be attributed to the decrease in the particles uniformity and increase in the surface roughness as shown in Fig. 3 (D-F). It is important to note that Ce doping did not result to change in morphology, thus, morphological property of ZnO NPs is unchanged in this study. Based on this analysis, both the FE-SEM micrographs and the statistical distributions confirm the formation of small average particle sizes that increases upon Ce doping while exhibiting spherical morphology.

3.3. EDX analysis for the undoped ZnO, 1Ce/ZnO and 3 Ce/ZnO NPs
The energy dispersive X-ray spectroscopy (EDX) was utilized to analyse the chemical compositions of the undoped ZnO, 1 Ce/ZnO and 3 Ce/ZnO NPs. The corresponding percent compositions for each individual constituent are listed in Table 2. The percent chemical compositions of Zn and O atoms, which are the main building blocks of the ZnO material, are presented in Table 2. The EDX data also shows the presence of Ce atom as shown in Table 2. The formation of relatively 1 to 1 ratio of Zn to O (Zn:O; 1:1) atoms in the whole samples indicates that the ZnO lattice distortion is minimized.

| S/NO | Element/ Symbol | Undoped ZnO | 1Ce/ZnO | 3Ce/ZnO |
|------|----------------|-------------|----------|----------|
| 1    | Oxygen/O       | 23.62       | 19.29    | 18.97    |
| 2    | Zinc /Zn       | 76.38       | 79.01    | 76.14    |
| 3    | Cerium/Ce      | -           | 1.70     | 4.89     |

4. UV Vis analysis
The absorbance measurements were carried out within 200 - 800 nm range to investigate the absorption properties of the prepared films for the undoped and Ce doped ZnO NPs. The absorption spectra for the undoped and Ce doped ZnO films show a very sharp absorption peaks as depicted in Fig. 4 (A). All the wavelength of the absorptions occurred below 400 nm with the undoped ZnO film occurring at 350 nm as shown in Fig. 4 (A). Doping 1 % Ce results to a slight shift to the higher wavelength (355 nm) indicating an increase in the photo-generated electron-hole pairs as well as change in band gap. Further increase in the Ce content to 3 % did not result to change in wavelength in the Ce/ZnO composite material. The measured absorbance values were used to estimate the direct energy band gap using the known Tauc equation [29].

\[ \alpha h \nu = A (h \nu - E_g)^{1/2} \]  

(8)

Where \( \alpha \), A, \( h \nu \) and \( E_g \) denote the absorption coefficient, constant, photon energy (eV), and energy band gap respectively. Extrapolation was done to obtain the \( E_g \) values on the photon energy axis (x-
The energy band gap of the undoped ZnO NP was found to be 2.69 eV as shown in Fig. 4 (B). This band gap was found to decrease upon 1 % Ce doping to 2.60 eV indicating a remarkable increase in the optical and electronic property of the undoped ZnO NPs. Koao et al. also reported similar result during their photocatalytic study using Ce doped ZnO nanoflower [30]. However, the energy band gap of the undoped ZnO film did not change upon further doping with 3 % Ce impurity as shown in Fig. 4 (B). It is obvious that the recorded energy band gap values are strongly correlated with the respective UV-Vis absorptions of the individual photocatalyst as displayed in Fig. 4 (A). Based on the band gap values recorded in this study, 1 Ce/ZnO film emerge as the optimum Ce doping due to its tendency to undergo a red shift and susceptibility to serve as a better photocatalyst among its analogues. This observed red shift exhibited by the 1 Ce/ZnO film may be ascribed to the presence of high absorption capacity, less amount of particles inter-growth as well as agglomeration as shown in Fig. 2 (B). The occurrence of such narrow energy band gaps exhibited by the undoped and Ce doped ZnO films indicate the presence of excellent optical and electronic properties. In comparison with literature, doping ZnO material with rare earth elements such as La, Eu and Dy were found to increase the energy band gap of ZnO material [16-18]. Possible reason could be attributed to the presence of Burstein-Moss Effect, a phenomenon that virtually results to a shift in the fermi level as a result of increase in a dopant concentration [16]. However, band gap reduction upon doping ZnO microstructure with Tb was also evident from literature [31].

Figure 4. (A) Absorption spectra and the (B) energy band gap for the undoped ZnO, 1 Ce/ZnO and 3 Ce/ZnO.

4.1. Photocatalytic study of the undoped ZnO, 1 Ce/ZnO, and 3 Ce/ZnO NPs

Figure 5. A representative absorption spectra vs. wavelength for the photocatalytic degradation of MB as a function of irradiation times in the presence of (A) undoped ZnO (B) Degradation efficiency for the undoped ZnO, 1 Ce/ZnO and 3 Ce/ZnO.
The photocatalytic degradation of 10 ppm MB dye took place under UV light irradiation between 5 - 100 min. The plots of the MB absorption spectra at the wavelength range between 200 - 800 nm for the undoped ZnO NPs has been presented in Fig. 5 (A). From the given photo-degradation absorption spectra, the most intense absorption bands occurred at 665 nm, which was within the range of the absorption λ_{max} commonly reported from literatures for MB degradation [8]. It could be observed clearly from Fig. 5 (A) that there is a very rapid photo-degradation achieved with respect to the undoped ZnO NPs. This could be seen from the decrease in the absorption band intensities as shown in Fig. 5 (D) presents the degradation efficiencies (DEs) of the undoped and Ce doped ZnO NPs, which compares the photocatalytic activities of the NPs during the photo-degradation period (5 – 100 min). The maximum estimated DE values achieved after 100 min of irradiation were found to be 63.58, 84.62, and 54.63 % corresponding to the undoped ZnO, 1Ce/ZnO, and 3 Ce/ZnO NPs, respectively. The trend in the increasing photocatalytic activity follows the order; 3 Ce/ZnO < undoped ZnO < 1 Ce/ZnO. This shows that, the 1 Ce/ZnO NPs demonstrates the highest photocatalytic activity. It could be noticed that 1 Ce/ZnO NP exhibited the most decreased and well separated MB absorption bands upon increasing irradiation time than the undoped and 3 Ce/ZnO NPs. This suggests the occurrence of a well efficient electron-hole pairs separation with the minimum possibility of electron-hole pairs recombination. The addition of Ce dopant into the lattice crystal of ZnO material could possibly enhance the structural and optical properties of the ZnO photocatalyst and will affect greatly the electronic properties of ZnO semiconductor (thirty two) [32]. Therefore, the presence of optimum level of Ce^{4+}/Ce^{3+} in the ZnO lattice could enhanced electron-hole pairs separation via trapping free electrons from the conduction band and subsequently increases photocatalytic activity [12]. From the chemical point of view of Ce metal having a variable oxidation states of +3 and +4, the presence of Ce^{4+} in the lattice structure of ZnO, may acts as an electron trapping agent by trapping temporarily the photo-generated electrons at the conduction band of ZnO, which could eventually enhances charge carriers separation [5]. The main rationale that led to the fastest and efficient photo-degradation achieved with 1 Ce/ZnO NP could be attributed to the reduced energy band gap and less agglomerated particles leading to a structurally enhanced surface that could efficiently slow down the recombination of electron-hole pairs and stabilizes the generation of the reactive radical species. Thus, the sudden reduction of energy band gap could eventually reduce the activation energy of the reaction and consequently enhance the photocatalytic activity [33]. Further increase in the amount of Ce (up to 3 %) in this study was found to decrease the undoped ZnO photocatalytic activity. Chang et al. also reported similar photocatalytic activity during their photocatalytic studies [34]. In comparison with literature, 1 % doping of other rare earth elements such as Nd into ZnO NPs demonstrated the highest degradation efficiency of 92 % under 300 min of UV light irradiation in the photo-degradation of MB dye [19]. Also doping 1 % of Eu^{3+} into ZnO NPs was found to exhibit the most efficient activity for tissue imaging in medicine [26]. Therefore, doping 1 % of a rare-earth element into the microstructure of ZnO NPs could open up a new avenue to synthesis of more efficient NPs that could be utilized in a number of applications.

4.2. Kinetics of the MB photocatalytic degradation in the presence of the undoped ZnO, 1 Ce/ZnO, and 3 Ce/ZnO NPs

The plots of the linear fittings of the ln [MB] vs. irradiation and the rate of reactions for the undoped and Ce doped ZnO NPs is depicted in Fig. 6 (A and B). The values of the rate constant (k) for the undoped and Ce doped ZnO samples were obtained from the slopes of the linear fittings of the plot of ln [MB] vs. irradiation time as shown in Fig. 6 (A). These rate constant values were found to be 9.09 x 10^{-3}, 21.10 x 10^{-3}, and 5.93 x 10^{-4}min^{-1} corresponding to the undoped, 1, and 3 Ce/ZnO NPs respectively. As shown in Fig. 6 (B), it could be seen that, 1 Ce/ZnO NPs gave the highest rate constant value of about 21.10 x 10^{-4} min^{-1}, hence its regarded as the most reactive and fastest photocatalyst for the MB photo-degradation achieved in this study.
4.3. Photo-degradation mechanism of methylene blue

In order to effectively evaluate the reactivity and capability of a given photo-catalysts, different catalyst compositions and reaction conditions were involved. In this study, MB dye was used as the model organic pollutant, whereas the undoped and Ce doped ZnO NPs were utilized as the photo-catalysts under UV light irradiation as a function of time. Herein, we discuss the mechanism of MB photo-degradation. ZnO is an n-type semiconductor that has a very rich defect chemistry due to the presence of dominant electrons contributed by the oxygen vacancies and Zn interstitials [29]. In the ZnO hexagonal wurtzite structure, Zn atom occupies half of the tetrahedral sites leaving the octahedral site empty. This shows that, ZnO is highly capable of accommodating both intrinsic defect and extrinsic dopant [29]. The overall photo-degradation mechanism depends on the degree of the MB dye adsorption on the surface of the photo-catalyst. The ability of the photo-generated electrons to migrate to the conduction band of ZnO semiconductor upon UV light irradiation facilitates the adsorption process as well as the formation of reactive species. The photocatalytic process begins by migration of electrons (e) from the valence band to the conduction band of the ZnO semiconductor material, leaving behind the photo-generated holes (h+) at the valence band upon UV light irradiation [35]. The molecular oxygen trapped the photo-generated electrons in the conduction band of ZnO, where it is then converted into the reactive oxygen species [5]. However, in the presence of Ce⁴⁺, the photo-generated electron is firstly temporarily trapped and thereafter transferred to the molecular oxygen to form the superoxide radical (O₂⁻), and the process is accompanied by reducing Ce⁴⁺ to Ce³⁺. This is because the lewis acidity of Ce⁴⁺ is theoretically superior to that of O₂ [16]. The O₂⁻ then reacts with water molecules (H₂O) to produce per-hydroxyl radical (HO₂⁻) and hydroxide ion (OH⁻) [20]. The HO₂⁻ rearranges to form molecular oxygen (O₂) and hydrogen peroxide (H₂O₂) [20] and finally the hydroxyl radical (OH⁻) was formed, which was subsequently utilized for the complete mineralization of the MB dye and eventually leading to the formation of CO₂ and H₂O and other possible mineralization products (MP). These could be expressed using the following chemical equations;

\[
\begin{align*}
\text{ZnO} + h\nu & \rightarrow e^- + h^+ \quad (9) \\
\text{Ce}^{4+} + e^- & \rightarrow \text{Ce}^{3+} \quad (10) \\
\text{Ce}^{3+} + \text{O}_2 & \rightarrow \text{Ce}^{4+} + \text{O}_2^- \quad (11) \\
\text{O}_2^- + \text{H}_2\text{O} & \rightarrow \text{OH}^- + \text{HO}_2^- \quad (12) \\
2\text{HO}_2^- & \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \quad (13) \\
\text{H}_2\text{O}_2 + \text{O}_2^- & \rightarrow \text{O}_2 + \text{OH}^- + \text{OH}^- \quad (14)
\end{align*}
\]
\[
\text{OH} + \text{MB} \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} + \text{MP} \quad (15)
\]

The results of the photo-degradation experiments revealed that the 1 Ce/ZnO NP is the optimum Ce doping utilized in this study for better MB photo-degradation. The utilization of such photocatalyst and its analogues may go along way solving the predicament associated with water pollutants and contaminants such as MB dye from any given aqueous solution or industrial effluent.

5. Conclusion
The synthesis and characterizations of the undoped, 1, and 3 Ce doped ZnO NPs using precipitation and deposition precipitation methods have been successful. NPs have been characterized using; XRD, SEM, EDX and UV-Vis. The photocatalytic degradation studies have been successfully carried out upon UV light irradiation as a function of irradiation time between 5 -100 min in the presence of the undoped and Ce doped ZnO NPs using MB dye as the model pollutant at RT. The results of the photocatalysis were found to be superb and promising. The most effective MB photocatalytic degradation occurred at 100 min photo-irradiation. The corresponding DE values were calculated to be 63.58, 84.62, and 54.63 % corresponding to the undoped, 1% and 3% Ce/ZnO NPs respectively. Possible reasons for the high photocatalytic activity associated with the 1 Ce/ZnO NPs, could be attributed to the presence of well-defined and less agglomerated particles and reduced energy gap. This study shows that rare-earth elements such as Ce could enhance the photocatalytic properties of the ZnO NPs when doped with an optimum amount. Therefore, doping 1 % of a rare-earth element into the microstructure of ZnO NPs could open up a new avenue to synthesis of more efficient NPs that could be utilized in a number of applications.

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