



Article Impact of Mo-Doping on the Structural, Optical, and Electrocatalytic Degradation of ZnO Nanoparticles: Novel Approach

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Abstract: Pure and Molybdenum (Mo)-doped zinc oxide (ZnO) nanoparticles were prepared by a cost-effective combustion synthesis route. XRD results revealed the decrement in crystallite size of ZnO with an increase in Mo-doping concentration. Optical bandgap (E_g) values were determined using optical reflectance spectra of these films measured in the range of 190–800 nm. The E_g values decreased with increasing the Mo-doping concentration. The dielectric properties of these samples were studied to determine the dielectric constant values. Raman spectra of these samples were recorded to know the structure. These sample absorption spectra were recorded for electrocatalytic applications. All the prepared samples were subjected to electrocatalytic degradation of Rhodamine B. The 0.01 wt% Mo doped ZnO showed 100% in 7 min electrocatalytic degradation.

Keywords: Mo-doped ZnO; nanostructured metal oxides; XRD/SEM; optical properties; electrocatalysis

1. Introduction

It is a known fact that all the world's human beings strongly depend on natural resources, for example, soil, water, air, etc. Unfortunately, in recent years, contamination of these resources has been very high from textile, leather, chemical laboratories, and paper industries, which were the primary sources of water pollution. They release unprocessed wastewater directly into the water bodies [1–4]. Using this unsafe water, many health problems will occur to human beings [1,5]. Currently, wastewater treatment and recycling are getting significant attention. Therefore, great attention has to be paid to investigating costeffective and eco-friendly techniques for water purification. Photocatalysis is a technique used for water purification that is simple and cheap. The importance of photocatalysis for water electrolysis and hydrogen fuel cells has been discussed by many researchers [6].

ZnO is one of the promising II–VI semiconducting materials, which displays a large optical band gap (3.37 eV) and exciton binding energy (60 meV), high linear refractive index, and electrical properties. These properties make ZnO suitable for electronics, photonic devices, UV laser diodes, piezoelectric transducers, light-emitting diodes sensors, solar



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). cells, and optoelectronic devices [7–11]. Semiconducting nanostructures with different morphologies such as nanoparticles, nanowires, nanorods, nanobelts, nanoprisms, nanodots, and nanostructured thin films help understand the physical and chemical properties of nanoscale systems. The behavior of electron, photon, and phonon of nanoscale systems was studied and reported by the earlier workers [12]. Different methods to fabricate ZnO nanoparticles include sol-gel, ultrasonic, chemical vapor deposition, microemulsion, organometallic precursor, solvothermal, microemulsion, and spray pyrolysis electrodeposition, sonochemical, microwave-assisted, and hydrothermal [13–21].

ZnO acts as a photocatalyst upon the photoirradiation by transferring electrons from the valence band to the conduction band in the shorter wavelength region [13,22]. Due to the similarities in the bandgap of ZnO and TiO₂, many researchers tried to replace expensiveTiO₂ photocatalyst with ZnO photocatalyst. Since ZnO is a low-cost and nontoxic material, it has received significant interest. Furthermore, during UV- light irradiation, ZnO exhibits remarkable electrocatalytic ability for degrading organic pollutants in aqueous suspension by generating powerful oxidizing agents such as hydroxyl radicals and superoxide radical anions, which decompose the organic pollutants [9], but they learned that ZnO is less active under visible light than TiO₂, and several attempts were made to improve ZnO properties.

The electrocatalytic activity of various ZnO crystal surfaces was investigated. They discovered that the surface atomic structures of the material had a significant impact on its photostability and electrocatalytic activity. When the surface is polar and has high surface energy, photolysis of ZnO occurs quickly [19]. Recently, reports enhanced electrocatalytic properties by adding dopants such as transition metals to ZnO lattice [13,23,24]. It is also reported that Mg-doped ZnO nanoparticles showed an adequate capacity to remove contaminating organic molecules, specifically MO (Ceramics International 47 (2021) 15668–15681). Recently, by introducing metal dopants, enhancement in electronic, magnetic, and catalytic properties of biphenylene network has been reported [25–28]. In the Mo-doped ZnO incorporation, Zn-O-M instead of Zn-O-Zn occurs, leading to new energy levels between the valence and conduction bands by lowering bandgap values. Mo-doped ZnO can be used as a photocatalyst to degrade bacteria and water purification [13,29]. Mo has an ionic radius similar to Zn^{2+} , which is a good match. As a result, it produces stable mixed metal oxides with the composition ZnO/MoO₃. Recently some workers also investigated the photocatalysis studies of Mo, Mn, Co, and Cu-doped ZnO thin films using different dye solutions and concluded that the pH of the dye solution plays a crucial role in the dye degrading mechanism [30].

In the current work, we demonstrated the synthesis of pure and Mo-doped ZnO nanoparticles by a cost-effective combustion synthesis method. The main objective of this study is pure, and Mo-doped ZnO samples were examined for water purification by using them as photocatalysts.

2. Experimental Details

2.1. Synthesis of Mo-Doped ZnO Nanostructures

The present study synthesized nanostructures of pure and Mo-doped ZnO using a low-cost combustion technique. As starting material, we prepared a homogeneous solution by adding 5gm of zinc nitrate (Zn (NO₃)₂.6H₂O) with 5 gm of citric acid in a crucible. Various concentrations of Ammonium pentamolybdate (0 wt%, 0.001 wt%, 0.01 wt%, 0.1 wt%, 0.5 wt%, and 1 wt%) with 30 mL of distilled water were added to the homogeneous solution. The solution was continuously stirred at 170 °C on a hot plate for 2 h. Finally, these solutions were heated in a furnace at 550 °C for 2 h; the final product is well-grounded using mortar and pestle. In the current study, six different samples were prepared by varying the concentration of ammonium pentamolybdate as 0 wt% (sample named ZNCM-1), 0.001 wt% (sample named ZNCM-2), 0.01 wt% (sample named ZNCM-3) 0.1 wt% (sample named as ZNCM-4), 0.5 wt% (sample named as ZNCM-5), and 1 wt% (sample named as ZNCM-6).

2.2. Devices and Measurements

The structural properties of the present samples were examined by using a Shimadzu LabX-XRD-6000 X-ray diffractometer, with CuK*a* = 1.54 Å radiation in the angle range from 5° to 80° .

The structural morphology of the present samples was investigated by scanning electron microscopy techniques (SEM-Jeol. JSM-6360 type) operated at 20 kV.

Optical reflectance (190–800 nm) and the absorption spectra (200–1600 nm) were recorded using a 3600 UV/Vis/NIR spectrophotometer (Shimadzu, Japan).

The present sample's Raman spectra were recorded using an FT-Raman spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). In addition, Fourier transforms infrared (FT-IR) spectra (400 to 4000 cm⁻¹) of the prepared samples were recorded by XDR FT-IR Spectrometer, THERMO SCIENTIFIC.

The dielectric properties were recorded using Keithley 4200-SCS in the frequency range of 1 kHz and 10 MHz.

A Rhodamine B dye (50 mg/L) was used as a typical organic pollutant in the experiment of electrocatalytic degradation. The electrocatalytic degradation processes and electrocatalysis single-cell reactor (EC) reactor were used, with 0.01 gm of catalyst provided and two graphite electrodes functioning as a working electrode and a counter electrode. The electrodes were separated by 5 cm under biasing DC voltage of 10 volts.

3. Results and Discussion

3.1. X-ray Diffraction Studies

The X-ray diffraction patterns of pure (ZNCM-1) and Mo-doped (ZNCM-2, ZNCM-3, ZNCM-4, ZNCM-5, and ZNCM-6) ZnO nanoparticles samples are demonstrated in Figure 1. The diffraction peaks of the ZNCM-1 sample matched with hexagonal ZnO structure. These peaks were indexed according to COD Card entry 9004179. We did not find any significant Mo or Zn residues from the XRD patterns of ZNCM-2 and ZNCM-3 samples. It indicates that Mo replaces Zn in the hexagonal ZnO lattice. Similar results were obtained for Mo and Al-doped ZnO and Mo-doped In₂O₃ films [31–39]. Further, the intensity of all the ZnO peaks decreased, whereas the intensity of Mo-based Mo5O14 peaks increased with an increase in dopant concentration observed in the XRD pattern of ZNCM-4, ZNCM-5, and ZNCM-6 samples. The peaks corresponding to Mo5O14 are indexed according to COD Card entry 1537518. K. Ravichandran et al. [1] reported similar results. The unit cell parameters of hexagonal ZnO calculated from the XRD pattern were $a = 3.2 \pm 0.2$ Å and $c = 5.2 \pm 0.2$ Å, indicating independence of dopant concentration of the samples. Scherer's formula was used to calculate crystallite size (*D*), dislocation density (δ), and dislocation density (δ), using the following relationships [21,22]:

$$D = 0.9\lambda/\beta\cos\theta \tag{1}$$

$$\delta = 1/D^2 \tag{2}$$

$$\varepsilon = \beta \cos \theta / 4 \tag{3}$$

Here, θ is the diffraction angle, λ is the X-ray wavelength in the nm unit, and $|\hat{A}|$ is the full width at half maximum (FWHM). All the calculated structural parameters of the present samples are depicted in Table 1. The average D value ZnO peaks [34] was 23 ± 2 nm for the samples ZNCM-1 and ZNCM-2. The D of ZNCM-3, ZNCM-4 and ZNCM-5 are 18 ± 2 nm. However, ZNCM-6 had a *D* of 14 ± 2 nm. The lower *D*-value for ZNCM-6 can be attributed to residues in the XRD pattern and lower the intensity of the ZnO peaks. It is clear that with increasing dopant concentration *D*-value of ZnO decreases. At the same time, ε and δ values increase with increasing Mo-dopants in the host ZnO material. The value of δ determines a defect density in a crystal, which arises due to misregistration of the lattice in one segment of another crystal section. Khalid Umar et al. (2015) observed similar results on Mo and Mn-doped ZnO and their electrocatalytic activity studies, and the possible



reason for decreasing crystallite size discussed as the addition of dopant may hinder the growth of ZnO particles [35].

Figure 1. XRD patterns of pure and Mo-doped ZnO nanoparticle samples.

 Table 1. The structural parameters of the pure and Mo-doped ZnO nanoparticles.

Sample		20	FWHM	d-Spacing	<i>a</i> , (nm)	<i>c,</i> (nm)	<i>D</i> , (nm)	$\mathbf{A} \times 10^{-3}$	δ ($ imes 10^{-15}$)
ZNCM-1 (0 wt% Mo)	ZnO	36.316 (101)	0.3738	2.47177	3.2445	5.1979	23.37	5	1.831
ZNCM-2 (0.001 wt% Mo)	ZnO	36.338 (101)	0.3789	2.47035	3.2425	5.1956	23.06	5	1.881
ZNCM-3 (0.01 wt% Mo)	ZnO	36.262 (101)	0.4800	2.47531	3.2494	5.2038	18.2	6.4	3.019
ZNCM-4 (0.1 wt% Mo)	ZnO	36.303 (101)	0.4800	2.47263	3.24523	5.2017	18.2	6.4	3.019
	Mo ₅ O ₁₄	32.484 (601)	0.5200	2.75408	23.0115	3.9571	16.63	7.8	3.616
ZNCM-5 (0.5 wt% Mo)	ZnO	31.773 (100)	0.4399	2.81406	3.2494	5.2038	19.62	6.7	2.597
	Mo ₅ O ₁₄	32.570 (601)	0.4144	2.7470	22.8809	3.9334	20.87	6.2	2.296
ZNCM-6 (1.0 wt% Mo)	ZnO	31.945 (100)	0.5836	2.79931	3.2323	5.1795	14.8	8.9	4.565
	Mo_5O_{14}	32.708 (601)	0.3600	2.7357	23.0176	3.9108	24.03	5.4	1.732

3.2. SEM Studies

The microstructure of prepared nano samples is displayed in Figure 2. All the microstructures exhibit highly agglomerated and soapy porous structures. The reason for this kind of structure is released out of the reaction mixture during combustion. Upon increasing dopant concentration, the size of the nanoparticles is reduced from 177, 168, 165, 154, to 135 nm for the samples ZNCM-1, ZNCM-2, ZNCM-3, ZNCM-4, to ZNCM-5, respectively. The same results were observed in the earlier reports [35–38]. There is a remarkable change in the microstructure of 1 wt% of Mo-doped ZnO sample (ZNCM-6) instead of having nanoparticles. This could be due to the occupation of Mo- in the additional interstitial site

of ZnO [35–40]. Petronela Pascariu et al. [41] reported platelet structured microparticles of diameters between 4 and 5 μ m for molybdenum oxide. In the present study, the microstructure of ZNCM-6 exhibits a nanoflakes structure. The observed nanoflakes are typical of the order of 300 nm few μ m. It was observed that the specific surface area of Mo-doped ZnO samples increases slightly with increasing Mo concentration, which may be due to a decrease in *D*-values. Due to the large surface area, these samples are suitable for the electrocatalytic activity of ZnO by adsorption of a dye [39,41]



Figure 2. SEM images (a) ZNCM-1, (b) ZNCM-2, (c) ZNCM-3, (d) ZNCM-4, (e) ZNCM-5, and (f) ZNCM-6.

3.3. Diffuse Reflectance Analysis of Mo-Doped ZnO Nanostructures

The Optical Diffuse Reflectance (ODR) spectroscopy is a specialized optical technique for determining the electronic structure of nanostructured materials. Reflection from the loaded samples generated by diffuse illumination is well studied because of its non-destructive nature and ability to generate a mirror-like reflection from loaded samples. To determine the optical bandgap and absorption coefficient of semiconducting material, the ODR technique is used. ODR of undoped and Mo-doped ZnO nanoparticle samples as a function of light wavelength in the range of 200–800 nm are shown in Figure 3. To summarize, the optical bandgaps are produced by the absorption of light through the nanomaterial; the optical energy band gap was calculated using the Kubelka–Munk model [42], which is as follows:

$$F(R) = \frac{\left(1 - R^2\right)}{2R} \tag{4}$$

where F(R) is the Kubelka–Munk function, and R is the absolute reflectance. The absorption coefficient (α) is calculated by the following equation [21,22]:

$$\alpha = \frac{absorbance}{t} = \frac{F(R)}{t} \tag{5}$$

where *t* is the height of the sample holder, which is equal to 2 mm, and the optical bandgap (E_g) is calculated from the following equation:

$$\alpha h\vartheta = \left(\frac{(F(R)h\vartheta)}{t}\right)^n = A\left(h\vartheta - E_g\right)^n \tag{6}$$

where h is the photon energy, $|\hat{O}|$ is the photon frequency, h is Planck's constant, and A is the band tailing factor, has values ranging from 1×10^5 to 1×10^6 cm⁻¹·eV⁻¹. The optical transition (n) values equal 1/2 for the direct bandgap, and the plots (optical band) are shown in Figure 4. The reflectance spectra of all samples were found to be identical in the wavelength range of 200–370 nm. The optical bandgap of the samples was revealed by a sharp increase in the ODR spectra between 370 and 410 nm. In the visible region of 410–800 nm, all ZnO nanoparticles have a high reflectance. ZNCM-1, ZNCM-2, ZNCM-3, ZNCM-4, ZNCM-5, and ZNCM-6 have estimated band gap values of 3.261, 3.259, 3.252, 3.256, 3.246, and 3.235 eV, respectively. E.g., values decrease as Mo-doping concentration increases, which could be due to new energy states between the valence and conduction bands. C. Aydn et al. [43] obtained comparable results for sol-gel prepared ZnO: Fe nanoparticles. ZnO nanoparticles have high reflectance values in the visible region that decrease as dopant concentration increases, indicating that these samples are suitable for electrocatalytic applications under visible light irradiation. Similar decreasing band gap values were observed by Peyman Gholami et al. (2019) [44] on biochar-supported ZnO nanorods in the degradation of Gemifloxacin.



Figure 3. ODR spectra of pure and Mo-doped ZnO nano-samples.



Figure 4. Tauc's plots of pure and Mo-doped ZnO nano samples.

3.4. Raman Spectroscopy of Mo-Doped ZnO Nanostructures

Figure 5 depicts the Raman spectra of pure and Mo-doped ZnO samples. Wurtzite ZnO is an associate of the C6V (P63mc) space group, and its possible vibrational modes [6,37] include U opt = $A_1 + 2B_1 + E_1 + 2E_2$. A_1 , E_1 , and E_2 are Raman active, while B_1 is Raman prohibited. The Raman peaks are observed at 95cm⁻¹, 328, 431, 808, 843, and 903 cm⁻¹, corresponding to E_2 low, E_{2H} – E_{2L} , E_2 high, E_2 low + A_1 (TO), E_2 high + A_1 (TO), and A_1 mode, respectively. These findings corroborated previous findings [7,45–49]. A_1 and E_1 are polar modes that are both infrared and Raman active, whereas E_2 is non-polar and only Raman active. E_2 high is the peak at 431 cm⁻¹. Wurtzite ZnO's characteristic peak indicates good crystallinity [50]. The intensity of the E_2 high mode decreases as dopant concentration increases, whereas the intensity of the A_1 mode increases.

3.5. FT-IR Spectroscopy of Mo-Doped ZnO Nanostructures

The types of bonds and functional groups present in pure and Mo-doped ZnO samples were investigated using FTIR spectra. Figure 6 depicts the FTIR spectra of pure and doped ZnO nanoparticle samples. Zn–O stretching vibration is responsible for the peak at around 440 cm⁻¹. Earlier researchers [51,52] reported characteristic peaks for MoO₃ at 553, 876, 995, 1630, and 3445 cm⁻¹. In the current study, we found one such peak at 809 cm⁻¹, and the intensity of this peak increases as dopant concentration increases. Peaks at 1462 and 1675 cm⁻¹ have previously been observed for ZnO nanoparticles and are attributed to asymmetrical and symmetrical stretching of the carboxylate group [53]. The stretching and bending vibrations of surface hydroxyl groups on ZnO were assigned to the peak at around 3280 cm⁻¹. The intensity of this peak increases as dopant concentration increases. These results agree well with the XRD results. The surface area of Mo-doped ZnO samples

ZNCM-6 ZNCM-5 Intensity, (a.u) ZNCM-4 ZNCM-3 ZNCM-2 ZNCM-1 600 800 1000 1200 200 400 Raman shift, (cm⁻¹)

increases, resulting in more hydroxyl groups on the samples' surfaces. The Hydroxyl group is important in dye decomposition because it transfers photogenerated holes (h+) to an OH radical [54].

Figure 5. Raman spectra of pure and Mo-doped ZnO nano samples.



Figure 6. FTIR spectra of pure and Mo-doped ZnO nanoparticle samples.

3.6. Dielectric Properties of Mo-Doped ZnO Nanostructures

The dielectric response of the ZnO nano is typically high compared to bulk materials. A surface with a large volume can produce micro-porosities, dangling bonds, and vacancy clusters. All these defects can alter the space charge distribution present in the sample. The electric field's positive and negative poles attract negative and positive space charge distributions in interfaces. The dipole moments are created when trapped at the defect site because the volume percentage of nano-size sample interfaces is more significant than bulk materials. Because of these essential properties of nanostructured material, the dielectric constant (ϵ_1), dielectric loss (tan δ), and total AC electrical conductivity ($\sigma_{AC.Total}$) for pure and Mo-doped ZnO nanomaterials in the range of 1 MHz–10 MHz are illustrated in Figure 7a–c, respectively, using the following equations [47,48]:

$$\varepsilon_1 = \frac{C \times l}{\varepsilon_0 \quad \times A} \tag{7}$$

$$\varepsilon_{2=} \tan \delta \times \varepsilon_1$$
, (8)

$$\sigma_{AC.Total} = \frac{\iota}{Z \times A'},\tag{9}$$

where the real part of the dielectric constant is ε_1 , and the imaginary component is ε_2 . *A* represents the electrode area, tan δ represents the loss tangent, *C*, *l*, and *Z* represents the sample capacitance, thickness, and impedance.

1

$$\sigma_{AC, Total} = \sigma_{DC} + B\omega^s$$
, where $\sigma_{AC} = B\omega^s$ (10)

The σ_{DC} denotes direct current conductivity, B is a constant, ω is the angular frequency, and s is a frequency exponent. The dielectric constant of the present samples decreased with increasing frequency and became saturated at higher frequencies (Figure 7a). The decreasing dielectric constant is explained as a high frequency, and the dipoles do not change in response to changes in the field variations. The decrease in dielectric constant values is caused by interfacial polarization/grain boundaries [40,41]. At lower frequencies, the dielectric constants of ZNCM-1, ZNCM-2, ZNCM-3, ZNCM-4, ZNCM-5, and ZNCM-6 are in the 40–48 range. The dielectric constant is frequency-dependent throughout the frequency range. It rises dramatically as the Mo content increases and stabilizes at high frequencies without significant change, allowing current samples to be used for various microwave device applications [46,55]. The frequency dependence of the dielectric loss with various concentrations of Mo is shown in Figure 7b. The dielectric loss also follows the same trend as the dielectric constant. It decreases with doping concentration at lower frequencies, indicating the dispersion phenomenon. It is worth mentioning that the dielectric constant and loss are purely dependent on Mo-doping concentration, suggesting that present samples found huge applications in microelectronic, sensors, and memory device applications. The electrical conductivity (σ_{AC}) gives a different Mo concentration with frequency variation, as shown in Figure 7c. From the figure, the conductivity is increasing with increasing frequency. The increase in conductivity suggests the clear influence of Mo doping in ZnO nanoparticles.



Figure 7. Cont.



Figure 7. (**a**) Dielectric constant, (**b**) dielectric loss, and (**c**) electrical conductivity of pure and Modoped ZnO nanoparticle samples.

3.7. Kinetic Study of Electrocatalysis of RhB of Mo-Doped ZnO Nanostructures

The electrocatalysis (EC) degradation of RhB dye was thoroughly investigated as a model organic species for the ZNCM electrode. To encourage charge carrier transfer via the external circuit, a voltage of 10 V was applied between the photoanode and cathode in the single-cell reactor. The data collected and recorded throughout the degradation show a

decrease in organic species absorbance with reaction time, indicating decreased organic species concentration. In the presence of seven different ZNCM samples, EC degraded RhB. As shown in Figure 8, EC degradation of RhB was consistent with previously reported pseudo-first-order kinetics [53,55,56].



$$ln(A/A_o) = -kt \tag{11}$$

Figure 8. Kinetic study of EC degradation of RhB in the presence of ZNCM nanoparticles.

The degradation efficiencies were computed using the relationship shown below [57]:

% of degradation =
$$(A_o - A_t/A_o) \times 100\%$$
 (12)

The initial absorbance is A_o . A_t is the absorbance at various time intervals is A_t , K is the rate constant value, and the reaction time is t. In the electrocatalytic reaction, a drop in the height of the absorbance peak at 525 nm wavelength was recorded with an increase in reaction time, providing a degradation efficiency of about 97 percent within 7 min, as shown in Figure 9. In the conduction band, excited electrons interact with electron acceptors to produce reactive species. As a result, the accumulation of electrons at the conduction band's bottom may slow charge carrier recombination even more. As a result, charge carrier separation is an excellent method for improving the electrocatalytic degradation of RhB [58]. RhB deterioration results demonstrate rapid ZNCM-3 over 7 min, as seen in Figure 9.



Figure 9. The % of EC degradation of RhB in the presence of ZNCM nanoparticles.

3.7.1. Mechanism of EC of RhB in the Presence of ZNCM

A significant benefit of EC is the influence of electrical energy, which results in better organic pollutant elimination efficiency [51]. Electrons are stimulated to the conduction band by electric charge, whereas empty holes reside in the valence band. When photogenerated holes interact with water molecules, they form powerful oxidants capable of breaking down refractory organic structures. Hydroxyl radicals are the second most powerful oxidants after fluorine due to their high standard reduction potential (Eo OH/H₂O) of approximately 2.8 V [59,60]. Unfortunately, photogenerated holes have a short lifetime due to their rapid recombination with electrons, a disadvantage in photocatalysis. However, in EC, an applied bias potential helps push photogenerated electrons away from the anode surface, extending the lifetime of generated holes [61]. Because current creates more holes, more hydroxyl radicals can be generated inside the solution, causing organic molecules to mineralize faster. Other reactive oxygen species are produced inside the reaction system, and the holes and hydroxyl radicals attack organic compounds in EC, which contributes to the mineralization of organic molecules. Superoxide radicals and hydroperoxyl radicals are weaker oxidizing entities [62].

According to previous work, creating a gradient at the ZNCM surface efficiently isolates generated charge carriers, according to previous work [63]. Electrons from the valence band (VB) are stimulated to the conduction band after an electric path more significant than the Eg on the ZNCM, leaving holes in the VB. During the degradation process, electrons pass through the external circuit to counter electro, assisting in forming highly reactive superoxide anion radicals (O₂). The valance band holes oxidize water, producing OH radicals interacting with organic contaminants to create a less harmful response. In the case of ZNCM photocatalyst, the primary degradation species are O_2 and generated holes (depending on the bonding of the catalyst with the pollutant). The combined impact of electrocatalytic oxidation processes influences ZNCM degradation performance. As previously mentioned, the following were the probable processes of RhB [64] photodegradation utilizing ZNCM in the presence of EC as mentioned in Scheme 1 and the following equations:

 $O_2 + e^- \rightarrow^- O_2 \tag{13}$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 (14)

$$O_2 + e^- \rightarrow^- O_2 \tag{15}$$

$$^{-}O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 (16)

$$H_2O_2 + e^- \rightarrow OH + ^-OH \tag{17}$$

$$(OH/^{-}O_{2}) + RhB \rightarrow products$$
 (18)

$$(h^+/H_2O_2) + RhB \rightarrow CO_2 + H_2O \tag{19}$$



Scheme 1. EC degradation mechanism/cell.

3.7.2. Comparison of PEC of RhB in the Presence of ZNCM with Previous Work

Table 2 compares electrocatalytic degradation of RhB in the presence of ZNCM to other prior study samples, highlighting their contributions to the synthesis technique, electrocatalytic conditions, and RhB concentration under consideration. It was discovered that ZNCM-3 has the highest electron degradation of RhB, with a 0.4 min⁻¹ rate of degradation and 100% degradation in 7 min. Nabil et al. [65] found that CoFe₂O₄ thin films electrochemically degraded an aqueous solution of rhodamine B (RhB) at a rate of 99 percent within the first three minutes of reaction time. The trapping studies revealed that the dominant active species were hydroxyl radicals, which resulted in the rapid elimination of RhB at an initial concentration of 10 mg/L. Ali et al. [66] investigated the electrochemical oxidation of Rhodamine B dye (RhB) on DSA and SnO₂ electrodes as active and non-active electrode models. They discovered that by using the DSA electrode in a NaCl 0.05 mol L1 + Na₂SO₄ 0.1 mol L1 solution as a supporting electrolyte, they could

achieve 100% color removal after 90 min of electrolysis. In various operating conditions, DSA outperformed SnO2 and was shown to be more cost-effective and efficient. Zhao et al. [67] concluded that using ZnWO₄ films as an anode resulted in a significant synergetic effect in rhodamine B (RhB) degradation via simultaneous electro-oxidation and photocatalysis. They discovered that RhB degradation follows the pseudo-first kinetic equation at bias potentials of 1.0, 1.5, and 2.0 V. The respective rate constants are 0.022, 0.026, and 0.138 hr⁻¹. Furthermore, as the bias increases, the rate of RhB degradation slows. There is almost no deterioration of RhB after the first hour at 3.5 V.

Table 2. The calculated data of rate constants of electrocatalytic degradation of Rhodamine B in the presence of **ZNCM** prepared samples with the previous work.

Samples	Synthesis Method	Dye Concentration	K_{r} (min ⁻¹)	% Removal	Refs.
ZNCM-1 (0 wt% Mo)	Combustion method	Rhodamine B (50 mg L^{-1})	0.2671	97% after 15 min	¥
ZNCM-2 (0.001 wt% Mo)	Combustion method	Rhodamine B (50 mgL $^{-1}$)	0.29064	98% after 15 min	10
ZNCM-3 (0.01 wt% Mo)	Combustion method	Rhodamine B (50 mgL $^{-1}$)	0.40605	100 % after 7 min	t t
ZNCM-4 (0.1 wt% Mo)	Combustion method	Rhodamine B (50 mg L^{-1})	0.31455	98 % after 15 min	en
ZNCM-5 (0.5 wt% Mo)	Combustion method	Rhodamine B (50 mgL $^{-1}$)	0.32801	97% after 15 min	res
ZNCM-6 (1.0 wt% Mo)	Combustion method	Rhodamine B (50 mgL $^{-1}$)	0.21218	96% after 15 min	Ь
CoFe ₂ O ₄	Electrodeposition	Rhodamine B (10 mgL $^{-1}$)		99% after 3 min	[65]
Ti/RuO ₂ -IrO ₂	DSA (De Nora Company)	Rhodamine B		100% after 90 min	[66]
ZnWO ₄	Dip-coating	Rhodamine B (5 mg L^{-1})	0.0023	after 60 min	[67]
$Ca_{10}(PO_4)_6(OH)_2$	Electrodeposition	Rhodamine B (5 mgL^{-1})	0.0399	98 % after 105 min	[68]
$Zn_3(PO_4)_2 \cdot _4H_2O$	Electrodeposition	Rhodamine B (30 mgL^{-1})		90 % after 10 min	[69]
TiO ₂ -NTs/Ce-PbO ₂	Electrodeposition	Rhodamine B (30 mgL^{-1})		90 % after 10 min	[70]
BiVO ₄ /TiO ₂	Sol-gel and hydrothermal	Rhodamine B (10 mgL^{-1})		93.9 % after 5 h	[71]

Furthermore, Ahmed et al. [68] electrodeposited hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ on stainless-steel substrates in aqueous solutions of calcium nitrate tetrahydrate and dihydrogen phosphate using the chronopotentiometry mode. They discovered that at time t = 105 min, the ratio Ct/Co decreases by 17% for a current density of 5 mA/cm² and by 98% for a current density of 30 mA/cm². A pseudo-first-order kinetics rule guided the degrading mechanism. Chennai et al. [69] discovered that $Zn_3(PO_4)2H_2O$ films (hydrated zinc phosphate, abbreviated h-ZP) are electrodeposited on different substrates and used as active anodes to electrode grade (RhB). It should be noted that after 12 min, the h-ZP/FTO electrodes have 90% RhB degradation. Qin Li et al. [70] developed cerium-doped lead dioxide (TiO2-NTs/Ce-PbO2) that degrades RhB 90 percent in 10 min. Wang et al. demonstrated improved electrocatalytic rhodamine B dye degradation [71]. The heterojunction was created using the sol-gel and hydrothermal methods. After a 5 h reaction time with an applied potential of 4.0 V, the degradation efficiency for eliminating rhodamine B dye was 93.9%.

4. Conclusions

In conclusion, pure and Mo-doped ZnO nanoparticles were prepared via the combustion route. With increasing Mo-dopant concentration, *D*-value of ZnO decreased. The microstructure of these samples exhibits a highly agglomerated and soapy porous structure. The ZnO nanoparticles exhibit high reflectance values in the visible region. The reflectance values of these samples decrease with the increase in dopant concentration. ZNCM-1, ZNCM-2, ZNCM-3, ZNCM-4, ZNCM-5, and ZNCM-6 have estimated band gap values of 3.261, 3.259, 3.252, 3.256, 3.246, and 3.235 eV, respectively. Eg values decrease as Mo-doping concentration increases. At lower frequencies, the dielectric constants of ZNCM-1, ZNCM-2, ZNCM-3, ZNCM-4, ZNCM-5, and ZNCM-6 are in the 40–48 range. In the case of ZNCM photocatalyst, the main degradation species are O₂ and generated holes (depending on the bonding of the catalyst with the pollutant). The combined impact of electrocatalytic oxidation processes influences ZNCM degradation performance. The dielectric constant is frequency-dependent throughout the frequency range. ZNCM-3 was a promising nanoparticle in EC of rhodamine b with 0.4 min^{-1} exhibited 100% degradation in 7 min.

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