Cost-Effective Efficient Materials for Dye Degradation using Green and Facile Chemistry Routes

Yogendra Yadawa (✉ pms19002@rgipt.ac.in)
Rajiv Gandhi Institute of Petroleum Technology

Divanshu Jha
Rajiv Gandhi Institute of Petroleum Technology

Nitesh Joshi
Rajiv Gandhi Institute of Petroleum Technology

Research Article

Keywords: ZnO, sol-gel route, Mg and S doping, photocatalysis, Rhodamine 6G degradation

Posted Date: August 24th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-3201553/v1

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Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on November 29th, 2023. See the published version at https://doi.org/10.1007/s11356-023-31036-z.
Abstract

In the present studies, the synthesis of Mg and S-doped ZnO nanoparticles was carried out using a non-aqueous sol-gel method. X-ray diffraction (XRD) techniques were used to examine the crystallisation of ZnO, Mg-ZnO, and S-ZnO samples. The Mg-ZnO and S-ZnO samples exhibit significant c-axis compression and smaller crystallite sizes as compared to undoped ZnO. To investigate the electronic, optical, and functional group characteristics of the nanoparticles, various spectroscopic techniques such as FTIR, X-ray photoelectron spectroscopy (XPS), UV/vis spectroscopy, and photoluminescence (PL) spectroscopy were employed. The optical band gap of Mg-ZnO and S-ZnO NPs were found to be 2.93 eV and 2.32 eV, respectively, which are lower than that of ZnO NPs (3.05 eV). The S-doped ZnO resulted in the homogenous distribution of sulfur ions in the ZnO lattice crystal. XPS analysis revealed that the doped S element was mostly $S^{4+}$ and $S^{6+}$. Furthermore, we investigated the photocatalytic activity of ZnO, Mg-ZnO, and S-ZnO samples with and without PVP mixed with 5 ppm Rhodamine 6G dye at room temperature. Results indicated that pure ZnO nanoparticles have the highest photocatalytic degradation rate with Rh 6G in both situations. The enhanced visible white light photocatalytic activities of pure ZnO NPs were attributed to their superior surface properties (18.30 m$^2$/g) and effective electron-hole separation.

Highlights

1. Magnesium (Mg) and sulphur (S) doped zinc oxide (ZnO) nanoparticles have easily synthesized using non aqueous sol-gel route.

2. The crystallite size of magnesium and sulphur doped ZnO particles have reduced due to the increment of lattice strain in the samples.

3. Sulphur doped zinc oxide (S-ZnO) samples has a flower-like nanosheet structure, which is responsible to reduce the band gap of pure ZnO nanoparticles.

4. The high surface area of spherical shape ZnO nanoparticles enhanced the photocatalytic activity of Rh 6G dye as compared to the Mg and S doped ZnO particles.

5. Polyvinylpyrrolidone (PVP) mixed ZnO, Mg-ZnO, and S-ZnO particles has reduce the photocatalytic activity of Rh 6G dye under visible light irradiation than the particles without PVP.

1. Introduction

Zinc oxide (ZnO) has a wide band gap of 3.37 eV and a large excitation binding energy of 60 meV at room temperature (Yang et al. 2017), making it a suitable candidate as a semiconducting material for vast applications in electronic and optoelectronic devices such as ultraviolet sensors (Capper et al. 2011), solar cells, laser diodes, gas, and biosensor (Mustafa et al. 2023; Giri et al. 2016; Al-Hardan et al. 2013; Zhao et al. 2010). In addition, ZnO exhibits high conductivity, high optical transparency, and thermal
stability (Zhan et al. 2013) in a hydrogen-rich environment (Lee et al. 2002). Recently, ZnO has emerged as a potential photocatalyst due to its high activity, high electron mobility, ability to reduce electron-hole pair recombination, low cost, and environmental stability features (Vinh et al. 2021). Modulating the bandgap energy of ZnO via a doping process has become an important task, as it can significantly alter the optical and electrical properties of ZnO. Several dopants such as aluminium, chromium, indium, and gallium have been successfully incorporated into ZnO for use in different applications such as gas sensors and transparent conductive layers. Magnesium-doped ZnO has been used in optoelectronic applications, including deep UV sensing (Minemoto et al. 2000; Ip et al. 2004). Many researchers have reported that non-metal doping with N, C, or S impurities can effectively modify the optical properties and electronic structure of intrinsic ZnO (Bai et al. 2012; Kumari et al. 2019; Debbichi et al. 2013). Among non-metal dopants, Sulphur (S) doped ZnO has more effective attention because of its size difference between S (1.84Å) and O (1.40Å) and high electronegativity (Yang et al. 2017). It leads additional oxygen and zinc vacancies to develop, which promotes O\(_2\) adsorption and the capture of photo-induced electrons, resulting in outstanding optical characteristics and high photocatalytic efficiency (Zhang et al. 2012). ZnO materials have been widely explored in this area and engineered into device solutions for challenges in numerous applications such as photocatalysis (Mekasuwandumrong et al. 2010; Khan et al. 2020), photocatalyst for water splitting (Maeda et al. 2010), photocatalytic degradation of water pollutants (Vasantharaj et al. 2021), UV photodetectors (Tian et al. 2014), heterogeneous catalysis (Rajesh et al. 2015), gas sensors (Jang et al. 2021), photovoltaic devices (Ravirajan et al. 2006), thin-film transistors (Lin et al. 2015), and more. The observed phases in ZnO have wurzite, zinc-blende, and rock salt (Wróbel et al. 2008; Yadawa et al. 2023) crystal structures.

The various types of materials that can be utilized for photovoltaic solar cells are mainly in the form of silicon (mono crystal, multi-crystalline, amorphous silicon), cadmium-telluride, copper-indium-gallium-selenide, and copper-indium-gallium-sulphide. In recent years, photovoltaic cell technology has grown significantly as a sustainable source of energy, driven by increasing concern over the impact of fossil fuel-based energy on global warming and climate change. First-generation solar cell refers to the p-n junction photovoltaic cell. That is made from silicon (multi-crystalline and single-crystalline) doped with other elements. Initially, materials like Germanium were used to make these solar cells. The first-generation photovoltaic cells, also known as silicon wafer-based solar cells, are the predominant technology in the commercial production of solar cells due to their high efficiencies and accounting for more than 86% of the solar cell market. However, they have high manufacturing costs (Swami et al. 2012). The second-generation solar cell, also known as a “Thin film solar cell”, offers a potential solution to the high cost of first-generation solar cells. While the efficiencies of thin-film solar cells are lower compared to silicon (wafer-based) solar cells, the manufacturing costs are also lower. Second-generation solar cells consist of several thin films, with light-absorbing layers that are generally only 1 µm thick, as opposed to the up to 350 µm thick layers found in silicon-wafer cells. The most successful second-generation materials include cadmium telluride (CdTe) (Chu et al. 1993), copper indium gallium selenide, amorphous silicon, and micro amorphous silicon. It consists of thin films of photon absorbers and layered stacks of thin films. The buffer layers are n-type materials with a larger band gap (low optical
absorption) than the absorber materials. In addition to high optical throughput, the layer should be thin in the range of 50–80 nm (Sinha et al. 2018) to maintain minimal series resistance.

In this study, we synthesized the ZnO NPs with a spherical shape, magnesium-doped ZnO nanoparticles with a large diameter microsphere shape, and sulphur-doped ZnO nanoparticles with a flower-like thin nanosheet structure using sol-gel methods. Herein, MgSO$_4$·7H$_2$O and NH$_2$CSNH$_2$ were used for the high-quality doping of Mg and S in parent ZnO nanoparticles. The doping of Mg and S atoms brought about significant changes in the surface morphology, crystallinity, and optical properties of the hexagonal wurtzite structure of ZnO nanoparticles. The synthesized Mg-ZnO and S-ZnO doping compounds were characterized using powder XRD, FTIR, FESEM, XPS, PL, and BET surface area analysers. Furthermore, ZnO, Mg-ZnO, and S-ZnO nanoparticles were utilized for the degradation of Rhodamine 6G (Rh 6G) dye in the presence of visible white light (LED) irradiation. Additionally, these particles were mixed in polyvinylpyrrolidone (PVP) polymer with ethanol to prepare an aqueous gel solution of PVP @ ZnO, PVP @ Mg-ZnO, and PVP @ S-ZnO for further photocatalytic degradation of the solution of the same concentration of Rh 6G dye under visible white light (LED) irradiation.

2. Experimental Procedure

2.1 Materials

Zinc acetate dihydrate (98%) was purchased from Sigma-Aldrich and it was used without further purification. Monoethanolamine (MEA) (100%, GR Merck) and ethanol were used as solvents. Magnesium (II) sulfate heptahydrate (MgSO$_4$·7H$_2$O) (99% extra pure, Sigma Aldrich), and thiourea (NH$_2$CSNH$_2$) (98.5% pure, Loba Chemie) were also acquired for the experiments. Di-ionized water was used throughout the experiments. The synthesized samples were stored in the desiccators, which attained vacuum utilizing lab scale mechanical pump. Analytical-grade glass beakers (Durasil) were utilized for the experiments. The pH of the solution was monitored and kept constant using a digital pH meter (Toschcon CL 54+).

2.2 Synthesis of ZnO, Mg-ZnO, and S-ZnO Nanoparticles from Sol-Gel Method

Zinc oxide (ZnO) sol was prepared as reported in our previous research paper (Yadawa et al. 2023) using the sol-gel method followed by doping magnesium and sulphur dopants into previously prepared ZnO to obtain the Mg-ZnO and S-ZnO nanoparticles. First, using Monoethanolamine as a stabilising agent, zinc acetate dihydrate (1.09 g) was mixed with 3.05 mL of Monoethanolamine at room temperature for 10 min. Then, 10 mL of ethanol was added as a solvent to the previous solution and stirred continuously at 60°C for 2 h to produce ZnO sol. To synthesize magnesium and sulfur-doped ZnO nanoparticles, 2 wt % of magnesium (II) sulphate heptahydrate was added for Mg-doped ZnO nanoparticles and 2 wt % of thiourea was added for S-doped ZnO nanoparticles to the previously prepared ZnO sol. The mixture was stirred for 2 h at 60°C. Initially, the solution was entirely transparent, but towards the end of the synthesis,
it turned milky white, confirming the synthesis of Mg-ZnO and S-ZnO nanoparticles. Mg-ZnO nanoparticles exhibited a yellowish-white powder colour, which aids in the creation of Mg-ZnO powder. After producing the ZnO, Mg-ZnO, and S-ZnO sols, they were allowed to be converted into gelation-type sol at room temperature for 12 hours before being preheated at 180°C for 1 hour and calcined in a muffle furnace at 500°C for 2 hours at a heating rate of 5°C/minute. Subsequently, these solid samples were crushed in mortar pastel to obtain a fine powder of ZnO, Mg-ZnO, and S-ZnO nanoparticles.

2.3 Characterization of Nanoparticles

2.3.1 Microstructural Characterization

A comprehensive investigation of the structural characterization of sol-gel synthesized ZnO, Mg and S-doped ZnO nanoparticles were carried out using Powder X-ray Diffractometer (EMPYREAN-QTY1, Malvern PANalytical, Netherlands). The PXRD measurements were carried out in the 2θ range of 20°–80° (step size of 0.003°) with Cu Kα (λ = 0.15406 nm) radiation. The qualitative elemental analysis was done by EDX, attached with FESEM (JSM-7900F, JEOL, JAPAN). Elemental mapping corresponding to BSE images was performed by EDXS. FESEM analysis, nanoparticles were gold (Au) coated (90 Sec) before introducing into the FESEM chamber. Accelerating voltage ranging from 5–10 kV was used to capture these images. For functional group tracing, FTIR analysis was performed (Spectrum Two, Perkin Elmer).

2.3.2 Optical Characterization

The Optical properties of synthesized nanoparticles were investigated using a UV-Vis NIR spectrophotometer (Cary 5000 with DRS 2500, Agilent Technologies) in the wavelength range of 200–800 nm to determine their absorbance and optical band gap. photoluminescence (PL) analysis was carried out in order to gain a deeper understanding of the surface characteristic of the nanoparticles. The PL emission spectra of nanoparticles were recorded by an Agilent Cary Eclipse spectrophotometer with an excitation wavelength of 277 nm. During PL analysis, the excitation and emission monochromators were positioned perpendicular to each other. To gain insight into the various states responsible for PL emission, the experimentally obtained spectra were subjected to multipeak Gaussian fitting.

2.3.3 Measurement of Photocatalytic Activity

We first perform the adsorption in the dark then photocatalytic degradation with a concentration of 5 PPM Rhodamine 6G (Rh 6G) dye aqueous solution in a custom-made jacketed transparent vessel. The photocatalytic reaction of metal oxide nanoparticles was carried out in a jacketed transparent reservoir which was custom-made. A double-walled glass chamber was attached with a LED light in the setup. To eliminate the influence of stray light, the complete assembly is housed inside a black box. Using a visible light source in the photocatalytic process, we used LED. To investigate the visible light photocatalytic activity of the produced adsorbents of ZnO, Mg-ZnO, and S-ZnO powders, an aqueous solution with a concentration of 5 PPM Rhodamine 6G was used. An aqueous solution of Rh 6G is exposed to light to investigate the kinetics of photocatalysis, and 2 ml of solution is taken out and centrifuged after each 30 minute interval. The centrifuged solution’s supernatant was collected and used for the UV-Vis
measurement. We studied the kinetics of degradation by measuring the concentration of Rh 6G with time and recording the characteristics of its peak at 526 nm wavelength.

3. Results and Discussion

3.1 X-ray Diffractogram of Powder Samples

Figure 1(a-c) shows the PXRD patterns of pure ZnO, Mg-ZnO and S-doped ZnO nanoparticles. The PXRD pattern of pure ZnO displays seven major peaks at 2θ values 31.88°, 34.57°, 36.36°, 47.71°, 56.80°, 63.09°, and 68.14°, which correspond to diffraction from (100), (002), (101), (102), (110), (103), and (112) planes respectively, as shown in Fig. 2(a). The XRD patterns align well with pure ZnO nanoparticles (JCPDS: 01-080-0075), with the hexagonal wurtzite structure (Abed et al. 2015; Garcia-Martinez et al. 1993; Hoggas et al. 2015). The lattice constants of pure ZnO were calculated to be a = b = 3.2539 Å and c = 5.2098 Å (Abed et al. 2015; Garcia-Martinez et al. 1993). The powder XRD shows a polycrystalline ZnO, Mg-ZnO and S-doped ZnO nanoparticles formation of the hexagonal wurtzite phase of ZnO, which can be indexed as a cubic system. The diffraction spectrum also shows that no additional secondary phases have formed with Mg dopant in the ZnO crystal lattice, and no substantial modifications are observed in the XRD pattern of the Mg-doped ZnO NPs. However, the intensity of the XRD peak decreases with Mg doping (shown in Fig. 1b) confirming the slender loss in crystallinity is due to the lattice distortion.

Doping of Mg$^{2+}$ ions into the crystal lattice of ZnO allows a minor amount of strain, which causes the lattice to exchange ions, resulting in a change in crystal regularity. However, very careful inferences indicate that the peak position shifts towards lower angle values as observed with Mg doping into the ZnO matrix, particularly for the peak located at (101) plane 36.36°, which is found to shift towards a lower value with Mg doping, which can be attributed to the replacement of Zn$^{2+}$ ions by Mg$^{2+}$ ions (Umaralikhan et al. 2017). It has been extensively established in the literature that the insertion of dopant materials changes the lattice properties of the host materials due to variations in the atomic radii of the host materials. Furthermore, dopant ions may substitute Zn$^{2+}$ ions in the host lattice of Mg$^{2+}$ ions (Talam et al. 2012). However, the basic structure of ZnO NPs remains unchanged, keeping their original wurtzite structure. This suggests that the majority of the Mg$^{2+}$ ions enter the lattice as substitution ions to replace the Zn$^{2+}$ ions and do not occupy the vacant regions. Because the ionic radius of the substituted dopant Mg$^{2+}$ (R = 0.57) is less than that of Zn$^{2+}$ (R = 0.60) (Labhane et al. 2015), the observed shift corresponds to a relatively small amount of lattice strain due to Mg$^{2+}$ entering ZnO.

Since the most intense peak of XRD can be ascribed as crystal growth with preferential orientation, we found the (100), (101), (102), (110) and (103) planes as the most intense planes in the X-ray diffraction pattern. Along the crystal plane of (101), magnesium (Mg) and sulfur (S) doping promotes grain size reduction from 19.458 nm to a minimum of 13.898 and 12.624 nm respectively (Yang et al. 2017; Yang et al. 2016). In both Mg and S doping elements, the grain size drops from the Scherer-Formula, indicating
that a larger amount of grain size change occurs in the case of S dopant because it may form an impurity phase instead of entering the lattice of ZnO nanostructures.

The crystallite size was calculated with the help of the Debye-Scherer equation (Perumal et al. 2015; Patterson et al. 1939).

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

Where \( \lambda \) is the wavelength of Cu-K\(_\alpha\) X rays (\( \lambda = 0.15406 \) nm), \( \beta \) is full width at half maxima (FWHM) of diffraction peaks and \( \theta \) is the diffraction angle. Although it is baffling to get exact values of crystallite sizes using the Debye-Scherer method, which is used to extract information on purely strain-related broadening.

### 3.2 Effect of Doping on Lattice Parameters

The physical properties of pure and doped ZnO NPs can be assessed by observing the crystallite size, lattice parameters, lattice strain, and dislocation density of the given sample (Manikandan et al. 2018; Raj et al. 2018). The lattice parameters of a wurtzite phase are calculated using Eq. (4), where \( a = b \) and \( c \) are the lattice parameters and \( d_{hkl} \) is the interplanar distance corresponding to its Miller indices (hkl). The lattice strain (\( \varepsilon \)) for pure ZnO, Mg-ZnO and S-ZnO were calculated by the following equation (Raj et al. 2018; Vargas et al. 2021).

\[
\varepsilon = \frac{\beta_{hkl} \cos \theta}{4}
\]

The variation in the average crystallite sizes and micro strains present in particles are measured by using the Williamson Hall equation (Mote et al. 2012) is demonstrated in Table 1.

\[
\beta_{hkl} \cos \theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin \theta
\]

Here, \( \beta_{hkl} \) is denoted as the full width at half maximum (FWHM), \( \theta \) is the Bragg diffraction angle, \( D \) is the average crystallite size (nm) in the direction perpendicular to the diffracting lattice planes, \( \lambda \) is the wavelength of the incident X-ray and \( \varepsilon \) is the average microstrain in the diffracting volume.

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

The lattice constant \( a = b \) and \( c \) for a plane (100) and (002) plane is calculated by (Vargas et al. 2021).
a = \frac{\lambda}{\sqrt{3 \sin(\theta)}} \quad (5)

c = \frac{\lambda}{\sin(\theta)} \quad (6)

The dislocation density (6) is calculated from Eq. (7) (Vargas et al. 2021).

\[ \delta = \frac{1}{D^2} \]

Table 1

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Crystallite Size (D) nm</th>
<th>FWHM ((\beta)) deg.</th>
<th>Lattice Parameters (Å)</th>
<th>Strain (%)</th>
<th>Dislocation Density ((6)) (\times 10^{-15}) (1/m²)</th>
<th>Williamson-Hall Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>19.458</td>
<td>0.4299</td>
<td>3.238</td>
<td>5.183</td>
<td>1.781</td>
<td>2.641</td>
</tr>
<tr>
<td>Mg-ZnO</td>
<td>13.898</td>
<td>0.6019</td>
<td>3.250</td>
<td>5.216</td>
<td>2.494</td>
<td>5.177</td>
</tr>
<tr>
<td>S-ZnO</td>
<td>12.624</td>
<td>0.6629</td>
<td>3.272</td>
<td>5.168</td>
<td>2.745</td>
<td>6.275</td>
</tr>
</tbody>
</table>

Table 1 shows that, when the Mg\(^{2+}\) ion replaces the Zn\(^{2+}\) ion in the lattice, the lattice parameter values increase. The increase in lattice parameters can be attributed to the elevation of crystal structure distortion monitored by Mg\(^{2+}\) incorporation. We calculated the lattice strain and found that the lattice strain increases after doping, causing distortion in the local crystal structure because of the differences in the atomic radius of Zn\(^{2+}\) (0.74 Å) (Perumal et al. 2015) and Mg\(^{2+}\) (0.57 Å) (Labhane et al. 2015).

Figure 2 shows a plot of as-prepared pure and dopant ZnO nanoparticles with 4sin\(\theta\) along the x-axis and \(\beta_{hkl} \cos\theta\) along the y-axis. The crystallite size was calculated from the y-intercept of the linear fit, and the strain was calculated from the slope of the fit. Eq. 3 represents the uniform deformation model (UDM) (Mote et al. 2012), in which the strain was considered to be uniform in all crystallographic directions, thereby accounting for the crystal's isotropic character. Therefore, material properties are unaffected by the direction in which they are measured.
4. Morphological Analysis

4.1 FESEM Images and EDX Analysis

Figure 3(a, d), (b, e), and (c, f) represent the FESEM analysis of sol-gel prepared ZnO, Mg-ZnO, and S-ZnO nanoparticles. These show the surface morphology at magnifications is 30,000 X and 50,000 X respectively. FESEM images of ZnO nanoparticles as seen to be spherical (Vishwakarma et al. 2020; Prajapati et al. 2023) with a size of 25 to 30 nm diameter.

From the FESEM images of Mg-doped ZnO nanoparticles, it is evident that the particles undergo surface aggregation and form a large number of regular microspheres with varying diameters in the range of 0.3 to 0.6 µm (Zhang et al. 2019). The aggregation of particles on the surface is attributed to the high surface energy of the synthesized Mg-doped ZnO nanoparticles (Roxy et al. 2021; Priscilla et al. 2021). The surface morphologies and microstructure of S-doped ZnO nanoparticles exhibit a flower-like nanosheet structure (Yang et al. 2017; Ardakani et al. 2018). These S-doped ZnO nanosheets possess well-defined hexagonal nanostructures with sharp edges and extremely narrow thicknesses of approximately 15 to 20 nm (Fujita et al. 2005).

Energy-dispersive X-ray spectroscopy (EDX) analysis was used to determine the chemical composition of the elements in ZnO, Mg-ZnO, and S-ZnO nanoparticles. The obtained EDX spectra of ZnO demonstrated the presence of various elements, with Zn (53.0%) and O (45.6%) being predominant elements, as depicted in Fig. 3(g). EDX spectra of Mg-doped ZnO nanoparticles clearly revealed the elemental composition of Zn (32.4%), O (58.4%), and Mg (9.2%) in [Fig. 3(h)]. From the EDX spectrum of S-doped ZnO nanostructures, its elemental composition was confirmed to be Zn (29.3%), O (52.1%), and S (18.7%) in [Fig. 3(i)]. It gives evidence of S atoms successfully incorporated into the ZnO nanostructures. The addition of Mg and S doping elements into the ZnO nanostructure changed the structural and optical properties of ZnO significantly.

4.1.1. Elemental Mapping Analysis

Figure 4(a-c) displays the mapping analysis of ZnO, Mg-doped ZnO, and S-doped ZnO nanostructures respectively. The distributions of these two elements like Zn and O are uniform in ZnO nanostructures. The dissemination concentration of O is smaller than that of Zn which is shown in Fig. 4(a). The Zn concentration in the mapping distribution of ZnO is greater than that of the EDX results. As a result, the results indicated that Zn is the main component of ZnO, and the O content is low but uniformly distributed on the surface of ZnO nanoparticles.

Figure 4(b) represents the mapping analysis of Mg-doped ZnO nanostructures, and the element Mg, Zn, and O are uniformly distributed on whole surfaces of ZnO. Mapping analysis of S-doped ZnO nanostructures also observed that the element Zn, S, and O are uniformly distributed on ZnO surfaces. Also, Fig. 4(c) showed the homogeneous distribution of the S element in the S-doped ZnO powders, and the S concentration is greater as compared with the Zn and O elements.
4.2 Fourier Transformed Infrared (FTIR) Spectra Analysis

Figures 5(a), and (b) represent the FT-IR spectra of as-prepared ZnO, Mg-ZnO and S-doped ZnO NPs in the range of 4000 – 700 cm\(^{-1}\) and 700 – 450 cm\(^{-1}\) wavenumber respectively. In the IR spectra of pure and doped ZnO samples wide band was observed due to the presence of hydroxyl group (-OH) at a wavenumber of 3450 cm\(^{-1}\). The composite nanoparticles exhibit several IR absorption peaks, which are the combination of the stretching bonds and bending vibrations of Zn–O, Zn-OH and Mg-ZnO (Vargas et al. 2021) in between the IR region of 600 – 450 cm\(^{-1}\) (Fig. 5b). Mg-ZnO and Mg-O bands are observed to present at a low wavenumber of 490, 498 and 602 cm\(^{-1}\) for the Mg-doped ZnO sample (Vargas et al. 2021). The IR spectra in Fig. 5(a) show that the doping of Mg and S atoms increased the intensity as well as the broadening of IR peaks with slight displacement in comparison to ZnO NPs. The change in the peak position indicated the successful incorporation of Mg and S into the hexagonal crystal structure of ZnO (Talam et al. 2012; Labhane et al. 2015).

4.3 UV–Vis diffuse reflectance spectra (DRS) and Energy Band Gap Calculation

The light absorption properties of synthesized ZnO-NPs with doping of Mg and S were obtained with a UV-Vis spectrophotometer in the wavelength range of 200–800 nm at room temperature (RT). Figure 6(a) shows the absorbance spectra of as-synthesized ZnO, Mg-ZnO, and S-ZnO samples at RT. The optical bandgap (\(E_g\)) was calculated using the Tauc method (Aga et al. 2022; Rana et al. 2015) indicated in Fig. 7(b-d). Typically, the optical band gap (\(E_g\)) for the synthesized ZnO, Mg and S-doped ZnO NPs could be obtained by plotting \((\alpha h\nu)^2\) versus \(h\nu\), where \(\alpha\) is the absorption coefficient, \(h\) is the Planck’s constant, \(\nu\) is the frequency of the radiation and \(h\nu\) is the photon energy. The calculated value of the energy band gap of ZnO, Mg-ZnO and S-doped ZnO NPs were 3.05, 2.93, and 2.32 eV respectively. Moreover, this flower-like nanosheet structure of sulphur doped ZnO (S-ZnO) particles has responsible to reduce the band gap from 3.05 eV to 2.32 eV.

The nanoparticles prepared from the sol-gel method show a red shift in the optical band gap, giving a value of Mg-doped ZnO and S-doped ZnO from 3.05 eV to 2.93 eV and 2.32 eV respectively. The decrease in bandgap might be attributed to the formation of defects with the introduction of doping elements (Zhuang et al. 2011; Zheng et al. 2007).

4.4 X-ray Photoelectron Spectroscopy (XPS) Analysis

The surface structure and chemical states of samples ZnO, Mg-ZnO, and S-doped ZnO were investigated using X-ray photoelectron spectroscopy (XPS), and the corresponding XPS elemental spectra are shown in Fig. 7(a-d). Zn 2p XPS spectra are shown in Fig. 7(a) for ZnO, Mg and S-doped ZnO nanopowder. The two well-defined XPS peaks of Zn 2p can be seen at 1021.87 eV and 1044.97 eV in pure ZnO attributing to \(2p_{3/2}\) and \(2p_{1/2}\) spin-orbit interaction. The B.E difference in the corresponding two peaks is 23.1 eV which indicates that the Zn atom is in a +2-oxidation state (Zhang et al. 2019; Wu et al. 2017). But in the
case of Mg-ZnO and S-ZnO samples, Zn 2p XPS spectra slightly shifted towards the higher binding energy with diminished peak intensity. In Fig. 7(b) the O 1s peak of the high-resolution spectrum were Gaussian fitted into two peaks of O1 and O2 in the pure ZnO sample.

The highest binding energy peak of O1s spectra in pure ZnO sample is centred at around 530.57 eV (O1), which can be attributed to the presence of O^{2-} ions within the hexagonal wurtzite structure of ZnO. Additionally, deconvoluted broad peak spectra at approximately 532.09 eV (O2), which can be attributed to the presence of hydroxyl group (OH^-) on the surface of ZnO (Chen et al. 2000). Conversely, the O1s XPS spectra of the Mg and S-doped sample is deconvoluted into only one peak at around 532.42 eV and 532.11 eV respectively, which can be attributed to hydroxyl groups (OH^-) are presented on the surface of the ZnO (Chen et al. 2000). From Fig. 7(c), it can be obtained that the bonding energy peak for Mg 1s in Mg-doped ZnO is 1305.31 eV, and Mg can be expected to be in the +2-oxidation state (Aksoy et al. 2012). Figure 7(d) shows the two well-defined S2p core level peak spectra in the form of S2p_{3/2} and S2p_{1/2} respectively. These S2p_{3/2} spectra were deconvoluted into the two peaks at around 161.91 eV for S^{2-} ions and 163.15 eV for sulphur-related compound SO_2 respectively while another higher binding energy S2p_{1/2} peak spectra deconvoluted into two peaks at around 168.88 eV and 169.66 eV, which is related to sulphate ion (SO_4^{2-}) respectively (Rodriguez et al. 1999).

4.5 Photoluminescence (PL) Spectroscopy

The photoluminescence emission spectra have been affected by numerous aspects such as inter-level separation of the electronic states, lifetimes, charge transfer, and separation efficiency of the photogenerated carriers (Wu et al. 2017). Figure 8 shows a comparison of emission spectra recorded in the visible region of calcined powders of zinc oxide, Mg-doped ZnO, and S-doped ZnO nanopowders generated by the bulk sol-gel method. In the visible region, two emission bands have been observed, one at 487 nm and the other around 523 nm. The second band can be attributed to the transition from the conduction band to the valence band since the energy (~2.37 eV) is close to the band gap calculated using the previously presented DRS data (~2.32 eV). The PL emission intensity of Mg-doped ZnO is greater as compared to pure ZnO, indicating the presence of more surface oxygen vacancies of the Mg-ZnO. Conversely in the case of S-doped ZnO nanoparticles reduction in PL emission intensity can be attributed to enhanced carrier lifetime (Mirzaeifard et al. 2020), suggesting the sulphur-doped ZnO nanoparticles have longer-lived carriers.

4.6 BET Surface Area Analysis

The specific surface area (S_{BET}), average pore diameter (BJH), and pore volume of sample ZnO, Mg-ZnO, and S-doped ZnO nanoparticles were determined by N_2 adsorption. Figure 9(a) displays the N_2 adsorption-desorption isotherms and (b) pore size distribution of sample ZnO, Mg-ZnO, and S-ZnO respectively. The isotherm indicates that the microspores are filled with the N_2 gas at extremely low pressure.
Table 2 demonstrated the diminished specific surface area, pore diameter, and pore volume of magnesium and sulphur-doped samples Mg-ZnO (13 m$^2$/g), and S-ZnO (5 m$^2$/g) as compared with pure ZnO (18 m$^2$/g) (Sivakami et al. 2016). The reduction of specific surface area, pore diameter and pore volume because of the agglomeration of Mg-doped ZnO nanoparticles to form a regular microsphere structure.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Diameter (nm)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>18</td>
<td>23</td>
<td>0.1228</td>
</tr>
<tr>
<td>Mg-ZnO</td>
<td>13</td>
<td>28</td>
<td>0.0810</td>
</tr>
<tr>
<td>S-ZnO</td>
<td>5</td>
<td>6</td>
<td>0.0036</td>
</tr>
</tbody>
</table>

### Table 2

Textural Properties of ZnO, Mg-ZnO and S-doped ZnO Samples Calcined at 500°C.

5. Photocatalytic Activity Studies

A high surface area facilitates the adsorption of reaction molecules, while small, spherical particle sizes are beneficial for minimising internal diffusion resistances of molecules (Wang et al. 2008). To demonstrate the effect of higher absorption in low wavelength regions, we performed the degradation of Rhodamine 6G (Rh 6G) dye in the presence of visible light at constant room temperature (RT) in the presence of ZnO, Mg-ZnO, and S-ZnO catalyst samples. Figure 10(a-c) shows the UV absorption spectra of dye solutions after being exposed to visible light (LED, 87 luminescence intensity) in the presence of nanoparticle samples at various time intervals. These data show that dye degradation is effective, as the intensity of the absorption peaks decreases with time.

The reaction kinetics of Rhodamine 6G (Rh 6G) degradation with photocatalyst was investigated by the Langmuir-Hinshelwood model (Perween et al. 2017), shown in Eq. 8.

$$-\ln(C/C_0) = kt$$ (8)

Here, $k$ is the reaction rate constant in (min$^{-1}$). The rate constants plots have been deduced from $\ln(C/C_0)$, (where $C$ and $C_0$ are the instantaneous and initial concentrations of Rh 6G respectively) versus irradiation time ($t$) curve by linear fitting. The kinetics curves for the decay of the signal at a corresponding peak wavelength ($\lambda = 526$ nm) with time (up to nine hours) are presented in Fig. 10(d).

The degradation kinetics rate of ZnO nanoparticles ($k_{\text{ZnO}} = 0.00344$ min$^{-1}$) is approximately 3.2 times faster than the Mg and S-doped ZnO particles because the specific surface area of the pure ZnO nanoparticles is higher as compared to the doped nanoparticles.

Moreover, we have also demonstrated the photocatalysis behaviours of polyvinylpyrrolidone (PVP) mixed ZnO, Mg-ZnO, and S-ZnO nanoparticles of an aqueous solution of Rh 6G dye in the presence of visible
white light (LED) at constant room temperature (RT).

Figure 11(a-c) depicts the UV absorption spectra of dye solutions after exposing them to visible light in the presence of PVP-mixed nanoparticles at various time intervals. The dye degradation is visible in these curves as the intensity of the absorption peaks decreases with time. The kinetics study of the PVP mixed nanoparticles with an aqueous solution of Rh 6G dye for the decay of the signal at a corresponding peak wavelength (λ = 526 nm) with time (up to nine hours) is presented in Fig. 11(d).

The degradation rate constant of the PVP @ ZnO sample ($k_{PVP@ZnO} = 0.00212 \text{ min}^{-1}$) is approximately 5.7 times faster than the polymer mixed PVP @ Mg-ZnO and PVP @ S-ZnO samples. Moreover, the degradation rate constant of PVP mixed magnesium and sulfur-doped ZnO samples, both are approximately the same as ($k_{PVP@Mg-ZnO} = 0.000369 \text{ min}^{-1}$), and ($k_{PVP@S-ZnO} = 0.000370 \text{ min}^{-1}$) respectively. Therefore, the effect of PVP mixed in ZnO, Mg-ZnO, and S-doped ZnO particles has not been effective to improve the degradation rate kinetics of the aqueous solution of Rh 6G at Room temperature.

6. Conclusion

Magnesium and sulfur-doped zinc oxide (ZnO) nanoparticles can be easily synthesized using the non-aqueous sol-gel route. The XRD results confirm that the phase structure of ZnO is hexagonal, and the crystallite size (d) decreases with the doping of Mg and S atoms due to the development of lattice strain in the ZnO crystal lattice. The effect of Mg and S doping element in the ZnO crystal lattice resulted in a reduced energy band gap of Mg-ZnO (2.93 eV), and S-ZnO (2.32 eV) as compared to pure ZnO (3.05 eV) nanoparticles. The high surface area of spherical shape ZnO nanoparticles enhanced the photocatalytic activity of Rh 6G dye as compared to the Mg and S-doped ZnO particles. However, the photocatalytic performance of polyvinylpyrrolidone (PVP) mixed ZnO, Mg-ZnO, and S-ZnO particles is found to be less effective in degrading Rh 6G under visible white light irradiation than the particles without PVP.

Declarations

Acknowledgements

Authors gratefully acknowledge the CRF facility of RGIPT, Jais, Amethi, India for allowing us to use the powder XRD, FESEM, FTIR, XPS, UV-Vis characterization facilities and Dr. Shikha Singh and Prof. M S Balathanigaimani for using the PL and BET surface area characterization.

-Ethical Approval

On the behalf of me (Mr. Yogendra Yadawa) and all co-authors have allowed for ethical approval.

-Consent to Participate

Yes, allowed for consent to participate.
-Consent to Publish

Yes, allowed for consent to publish.

-Authors Contributions

Yogendra Yadawa: Conceptualization, Validation, Data Curation, Supervision, Writing-Original Draft with Review & Editing.

Divanshu Jha: Perform experiment, Collecting data and Characterization.

Nitesh Joshi: Perform experiment, Collecting data and Characterization.

-Funding

RGIPT institute departmental fund.

-Competing 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.

Mr. Yogendra Yadawa (On behalf of all co-authors)

Department of Chemical Engineering and Biochemical Engineering,

Rajiv Gandhi Institute of Petroleum Technology, Jais, Amethi, Uttar Pradesh-229304, India

References


35(7):1708–1716. https://doi.org/10.1364/JOSAB.35.001708


**Figures**
Figure 1

(a), (b) and (c) represent the powder X-ray diffractograms (XRD) of pure, Mg and S-doped ZnO NPs calcined at 500°C.

Figure 2

Williamson-Hall equation plot of $\beta_{hkl} \cos\theta$ vs $4\sin\theta$ of pure ZnO, Mg-ZnO and S-ZnO NPs.
Figure 3

(a, d), (b, e), and (d, f) shows the FE-SEM morphology of ZnO, Mg-ZnO, and S-ZnO NPs respectively at 30 and 50 kX magnification, and (g-i) shown EDX of ZnO, Mg and S-doped ZnO NPs respectively.

Figure 4

(a), (b) and (c) shows the elemental mapping of bulk powder ZnO, Mg and S-doped ZnO NPs respectively.
Figure 5

(a), and (b) represent the FT-IR spectra of ZnO, Mg-ZnO and S-doped ZnO nanoparticles.
Figure 6

(a) UV-Vis DRS data in terms of absorbance and (b-d) Tau-plots used for extracting the energy band gap of ZnO, Mg-ZnO, and S-ZnO NPs respectively.
Figure 7

(a) Zn2p\textsubscript{3/2} and (b) O1s XPS peaks of ZnO, Mg-ZnO and S-ZnO NPs and (c) Mg1s and (d) S2p\textsubscript{3/2} XPS peaks of Mg-doped and S-doped ZnO NPs.
Figure 8

Emission spectra of three samples recorded for two peaks in the range (i) 470-500 nm, and (ii) 510-540 nm.
Figure 9

(a) Nitrogen adsorption-desorption isotherms and (b) Pore size distribution of pure ZnO, Mg-ZnO and S-ZnO NPs, respectively.
Figure 10

(a-c) UV-Vis absorbance spectra and (d) Kinetics study of Rh 6G with ZnO, Mg-ZnO and S-ZnO NPs respectively under visible light irradiation.
Figure 11

(a-c) UV-Vis absorbance spectra and (d) Kinetics study of Rh 6G dye with PVP mixed nanoparticles under visible light irradiation.

Supplementary Files

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