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Short Communication

Facile Magnesium Doped Zinc Oxide Nanoparticle Fabrication and Characterization for Biological Benefits

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Abstract

Zinc oxide (ZnO) is the most common and widely utilized nanomaterial for biological applications due to their unique characteristics, such as biocompatibility, biosafety and antimicrobial along with thermal stability and mechanical strength. Magnesium (Cu) is considered as a significant dopant for ZnO due to their almost similar ionic radii and their role in biological activities which enhances the biological properties of ZnO. Thus, pure and magnesium doped nanocrystalline ZnO particles were synthesized through sol-gel approach in the current study. The concentration of the dopant is varied from (0.1% - 0.3%) and the composition, structural and optical characterizations were performed by using X-Ray Diffraction (XRD), Transmission Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectroscopy, UV-Vis optical absorption and photoluminescence (PL) spectrometer. The structural analysis confirmed that magnesium ions substitute Zn ions without altering their wurtzite structure with a high degree of crystallization. Morphological analysis confirmed that the magnesium doping process strongly influences the morphology of ZnO nanoparticles. PL measurement had been carried out at room temperature in which high intensity broad emission peaks were observed in the visible region around 450 - 700 nm that indicates the superposition of green emission bands. Thus, green photo luminescent magnesium doped ZnO nanoparticles from the current study are proposed to be highly beneficial as biosensors, photocatalysts and light-driven antibacterial agents.

Keywords: *ZnO nanoparticles, Magnesium dopants, Sol-gel approach, Photoluminescence, Wurtzite crystal.*

1. INRODUCTION

The deliberate addition of impurities into a polycrystalline material to modify their specific properties, is named as doping process. This process has become an usual technique in the fabrication of nano-particles to enhance their properties required for desired applications [1]. Especially in metal oxide nanoparticle synthesis, the introduction of metal ions as dopants are widely accepted to alter their intrinsic bandgap [2]. Generally, metal oxide nanoparticles possess narrow bandgap which makes them beneficial as semiconductor and photocatalyst [3-5]. The introduction of dopants will further enhance their electrical conductivity [6], photon absorption and release, due to the formation of dual stage bandgap [7]. Several other properties of the nano-particles are also engineered, as dopants alter their basic crystal structure and reduces bandgap, which eventually helps

to elevate the benefits of nanosized particles in industrial and biomedical applications [8, 9]. These doped-metal oxide nanoparticles can be classified into nitrogen- [10], carbon-, sulfur- [11], metal, metal oxide and complex ion doped particles [12, 13]. Among them, metal doped metal oxide nanoparticles are reported to be highly stable and reactive in aqueous medium, compared to other doped-nanoparticles [12, 14]. These metal doped-metal oxide nanoparticles are widely utilized as photocatalysts in wastewater treatment [15], solar cells [16] and photo-activated antimicrobial applications [17].

Nanosized zinc oxide (ZnO) particle is one of the metal oxide nanoparticle that are in high demand for several applications. They possess enhanced semiconductor, piezoelectric [18], electronic [6], thermal stability [19], optical and luminescent properties [20]. In addition, they are also less toxic towards various cell lines [21] and possess biological properties such as anticancer [22], antidiabetic [23], antimicrobial [24], anti-inflammatory [25] and as nanomedicine for various disease treatments [26]. In spite of all these properties, there are opportunities to further improve the properties of ZnO nanoparticles. Thus, dopants are introduced in ZnO nanoparticles, especially metal ions such as iron [27], magnesium [28], copper [29], aluminium [30] and rare earth elements [31]. Each of these metal dopants possesses unique ability to elevate the properties of ZnO nanoparticles, however, magnesium-doped (Mg-doped) ZnO nanoparticles are fabricated in the present work as it shows promising exclusive physicochemical properties for biological benefits [32], along with photocatalytic [28] and sensor applications [33].

Etacheri et al. (2012) reported Mg-doped ZnO nanoparticle synthesis via oxalate coprecipitation approach. The results showed that 0.2% of Mg-doped ZnO nanoparticles are about 50±5 nm after calcinating at 600°C [28]. Likewise, Kulandaisamy et al. (2016) demonstrated that the spray pyrolysis method can be utilized to form Mg-doped ZnO thin nanofilms. In this method, spherical shaped nanosized grains formed the thin films and a preheating of 250°C was required for the thin film formation [34]. Further, Arshad et al. (2015) fabricated Mg-doped ZnO nanoparticles using wet chemical sol-gel approach. In this study, chlorides of zinc and magnesium as precursor and dopant, respectively, and a calcination temperature of about 400°C for 4 hours was utilized to yield 13.5 nm sized Mg-doped ZnO nanoparticles [35]. Jiang et al. (2015) also synthesized Mg-doped ZnO nanoparticles via sol-gel approach using nitrates of zinc and magnesium to obtain 70 nm sized nanoparticles. A calcination temperature of about 650°C for 2 hours was employed in this method to obtain spherical shaped nanoparticles [36]. Thus, the present work is unique by utilizing novel sol-gel approach with zinc chloride and magnesium nitrate as precursor and dopant agent, respectively. Moreover, the formation of Mg-doped ZnO nanoparticles was carried out with aging and drying at 120°C for 24 h, without any calcination temperature, which is a major advantage in proposing this approach to fabricate nanoparticles for large-scale biological applications.

It is noteworthy that magnesium is one of the abundant metals in the world which is highly stable [37], thermally reactive [38], corrosion [39] and heat resistive in nature [40]. Further, it can be noted that magnesium has potential to combine with metals and metal oxides via simple and strong bond formation to elevate their stability and properties [35]. Furthermore, magnesium is highly beneficial as a co-factor for 300 enzymes, energy production, protein synthesis, oxidative phosphorylation, glycolysis and blood pressure regulation in humans and other living organisms [41]. Thus, the aim of the present work is to fabricate magnesium

doped zinc oxide nanoparticles via simple sol-gel approach and identify their effect of dopant concentration in the properties and characterization of ZnO nanoparticles. In addition, the current study reveals the photoluminescence and crystalline properties of Mg-doped ZnO nanoparticles and their possible biological benefits, in comparison with the green synthesized ZnO nanoparticles.

2. EXPERIMENTAL PROCEDURE

2.1. Materials and Methods

The synthesis of magnesium doped ZnO nanoparticle in this present work is performed via simple sol-gel procedure. The sol-gel synthesis involves anhydrous zinc chloride with ≥ 99.9 % purity and molecular weight of 136.31 g/mol (Sigma Aldrich, USA) as a precursor, ethanol as solvent with a molecular weight of 46.06 g/mol and 99.4% purity (Fisher scientific, Singapore) and sodium hydroxide pellets with a molecular weight of 39.997 g/mol and 97% purity (Sigma Aldrich, USA) as gelling agent was used for the formation of zinc hydroxide particles. The magnesium nitrate hexahydrate with 99.9% purity and molecular weight 295.6 g/mol (Sigma Aldrich, USA) is used as magnesium dopant. All the chemicals and reagents were of analytical gradient and used directly without any purification process.

2.2. Synthesis and Characterization of Magnesium Doped ZnO Nanoparticles

Initially, an equimolar ratio of zinc precursor and gelling agent (0.2 M) were dissolved in ethanol separately and were subjected to constant stirring for 2 h using a magnetic stirrer. After complete dissolution of powder particles in ethanol, both were mixed together in dropwise by stirring for an hour to modify their pH to 5 and to form a three-dimensional zinc gel network. During the process of gel formation, 0.1% of magnesium nitrate dissolved in ethanol is added via stirring for 2 h to dope magnesium with zinc gel mixture. The final product is centrifuged several times with distilled water and ethanol to remove excess chlorides, aged for 12 h and dried for 24 h at 120°C to remove the excess ethanol from the mixture and obtain pure magnesium doped ZnO nanoparticles [42, 43]. Figure 1 shows the schematics of the synthesis procedure used for the fabrication of magnesium doped ZnO nanoparticles. The possible chemical equation for the formation of Mg-doped ZnO particles via sol-gel approach was given in Equation 1-3. The same procedure was carried out to synthesize 0.2 and 0.3% of magnesium doped ZnO nanoparticles, whereas undoped ZnO nanoparticles were synthesized without the addition of magnesium nitrate during gel formation. The magnesium doped nanoparticles were characterized using UV-Visible spectrophotometer to study their optical properties and confirm the formation of ZnO nanoparticles with magnesium dopants, X-ray diffractometer (XRD) to study their crystallinity and phase shift due to dopants, Fourier Transform – Infrared (FTIR) spectroscopy to obtain the functional group in the sample, Scanning electron microscopy (SEM) to obtain their morphological information and photoluminescence spectroscopy to study their luminescence properties.

$ZnCl_2 + NaOH + C_2H_5OH \rightarrow ZnOH + Cl_2 + Na + C_2H_5OH$

(Equation – 1)

$ZnOH + Cl_2 + Na + C_2H_5OH + Mg(NO_3)_2$

↓

$Mg\text{-}ZnOH + Cl_2 + Na + C_2H_5OH + (NO_3)_2$

(Equation 2)

$Mg\text{-}ZnOH + Cl_2 + Na + C_2H_5OH + (NO_3)_2$

↓

Mg-ZnO powder (after aging and drying)

(Equation 3)

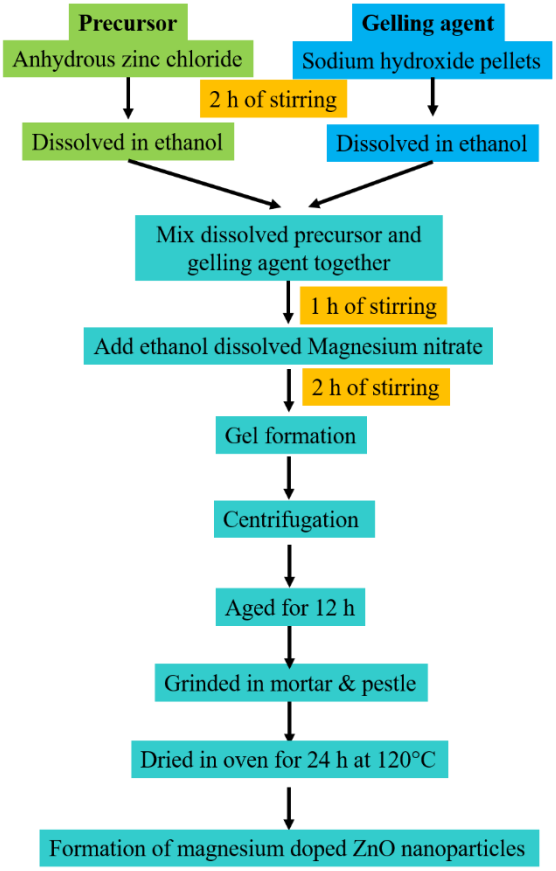

Figure 1. *Schematics of sol-gel mediated magnesium-doped ZnO nanoparticles synthesis.*

3. RESULT AND DISCUSSION

The obtained white colored powder, after the drying process, is predicted to be magnesium doped ZnO nanoparticles. The powder samples are processed using a mortar and pestle to obtain a fine powdered sample which was stored in a vacuum desiccator for further characterization studies.

3.1. Crystallinity of Pure and Doped ZnO

The X-ray diffraction spectral peaks of the fine powder sample as displayed in Figure 2 was obtained through Bruker® Advanced D8 X-ray diffractometer. The spectral data of undoped, pure ZnO powders were matched with the International Centre for Diffraction Data (ICDD) files to confirm their phase purity and crystallinity. The spectral peaks are exactly matching with the reference pattern of ICDD (01-070-8072) that corresponds to pure zinc oxide crystals of hexagonal wurtzite phase [44]. However, there exists certain impurity peaks which may be due to the unreacted and non-evaporated ethanol and hydroxide molecules that are present in between the zinc oxide crystals [45]. The XRD peaks of 0.1% of magnesium ion doped ZnO showed similar zinc oxide crystal peaks with less impurity peaks and certain peaks related to magnesium ions. It is noteworthy that the incorporation of magnesium dopants reduces the intensity of XRD peaks and leads to peak shifts which may be due to the overshadowing of zinc oxide diffraction by magnesium ions. The results are similar to the Mg-doped ZnO thin films prepared by Shan et al. (2004) [46]. Further, the XRD pattern of 0.2% and 0.3% of magnesium ion doped ZnO showed that the increasing dopant concentration elevates the peak intensity, especially the peaks related to magnesium ions. This clearly states that the introduction of 0.1% magnesium dopants into the zinc oxide crystals replaces the impurities which eventually starts to replace zinc ions in the zinc oxide crystals and creates void spaces to accommodate impurities at 0.2 and 0.3% of higher magnesium dopant concentration [35] as shown in Figure 3.

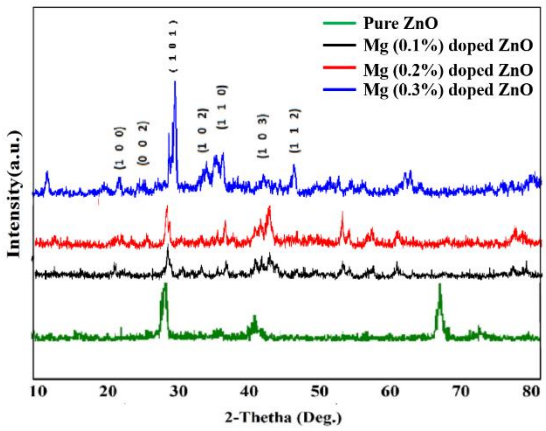

Figure 2. *XRD spectra of sol-gel synthesized pure and Mg-doped ZnO.*

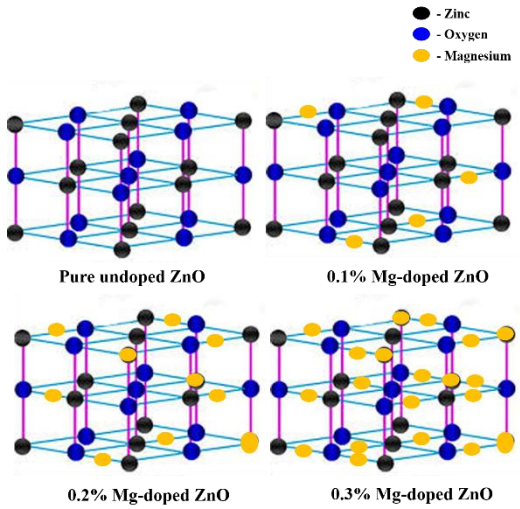

Figure 3. *Schematic representation of ZnO wurtzite crystal and 0.1-0.3% Mg-doped ZnO crystal structure.*

3.2. Optical Properties of Pure and Doped ZnO

The UV-visible absorbance spectra of the undoped ZnO and different concentration of magnesium doped ZnO are displayed in the Figure 4. The absorption spectra were obtained from 200 – 800 nm of wavelength by using Perkin Elmer® Lambda 25 UV-Vis spectrophotometer. The sharp peak at the wavelength of 230 nm shows the presence of oxide in the undoped ZnO powder sample, whereas the short peak at 385 nm is reported to be due to the presence of metal [47], which is zinc in the present study. The addition of magnesium dopants leads to a gradual increment in the absorption of ZnO, which is due to the incorporation of higher dopant concentration. However, there is no reduction in the peak that corresponds to metal ions which further supports that the magnesium dopants at higher concentration replaces zinc ions [48]. Moreover, the calculated bandgap energy from UV-visible spectrum for pure ZnO is 3.35 eV and the average bandgap energy for Mg-doped ZnO is ~3.44 eV. In a similar study by Zak et al. (2012), it has been proved that the crystallite size and the lattice strain in the ZnO crystals due to magnesium dopants leads to the peak broadening and increase in the peak that corresponds to metal and oxide [49].

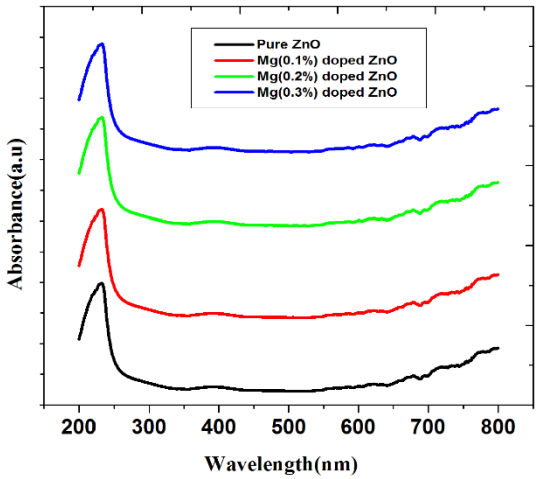

Figure 4. *UV-visible spectra of sol-gel synthesized pure ZnO and Mg-doped ZnO.*

3.3. Functional Group Analysis of Pure and Mg-doped ZnO

Figure 5 is the FTIR spectra obtained using Thermo scientific NICOLET iS10 instrument, which helps to predict the functional groups present in pure, undoped ZnO and Mg-doped ZnO. The FTIR peaks present at ~3500, 1400 and 1000 – 800 Cm^{-1}, exactly matches with the vibrational modes of O-H stretch, O-H ring stretches, C-O-H bending and metal oxide, respectively. The existence of these vibrational modes represents the presence of pure, undoped zinc oxide in the fine powdered sample along with functional groups such as carboxylic acid and hydroxide as capping agent that reduces the size of ZnO in the nano-regime [50]. The FTIR spectra of 0.1% magnesium doped ZnO sample are different from other magnesium doped samples which is due to the mixing of magnesium dopant precursor with the capping agent and impurities of ZnO mixture. However, the reduction in the peak intensity of the magnesium doped samples confirmed the presence of magnesium ions in the interstitial lattice positions of the ZnO crystals [51, 52]. The introduction of higher magnesium dopant concentration (0.2 and 0.3%) leads to an elevation in the peak intensity and shifts in the peak, confirms the replacement of zinc

ions with magnesium dopants in the zinc oxide wurtzite crystals [53, 54].

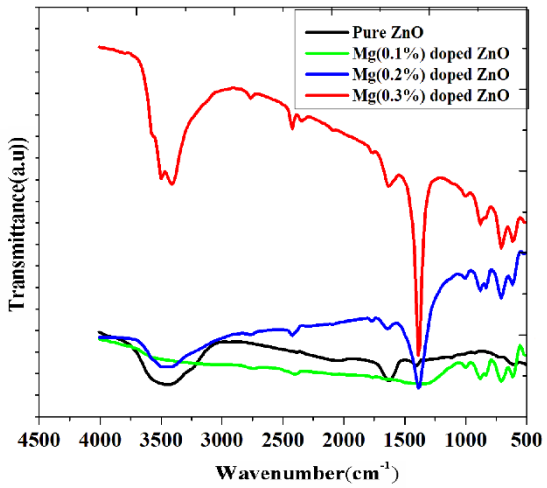

Figure 5. *FTIR spectra of sol-gel synthesized pure and Mg-doped ZnO.*

3.4. Morphological Analysis of Pure and Mg-doped ZnO

Figure 6 is the transmission electron micrograph of pure ZnO nanoparticles and different concentration of magnesium doped ZnO nanoparticle samples obtained from LIBRA®120 PLUS, Zeiss company. Figure 6 (A) and (B) reveals that the pure, undoped zinc oxides are in the range of 400 to 800 nm in size and are polydispersed with irregular spherical flake morphology. The results are similar to the ZnO synthesized via solid state reaction method [55]. However, the doping process of 0.1% magnesium ion concentration leads to the transformation of spherical flakes to spherical shapes as shown in **Figure 6** (C) and (D). This may be due to the lattice modifications due to the addition of magnesium ions to the interstitial position of zinc oxide crystals [56]. It is noteworthy that the particles start to agglomerate, even though the size is reduced, compared to undoped ZnO. The addition of 0.2% concentration of magnesium ions as dopant leads to further alterations in the agglomerated spherical shapes of Mg-doped ZnO into expanded spherical shapes as flakes as displayed in **Figure 6** (E) and (F). The expansion of nanoparticle can be attributed to the gradual replacement of zinc ions by magnesium dopants in the zinc crystals due to increased dopant concentration [36]. Furthermore, 0.3% concentration of magnesium ion doped ZnO leads to the smaller irregular spherical and hexagonal shaped particles in the size range 80 - 200 nm. This reduction in the size of doped ZnO nanoparticle can be attributed to the replacement of several zinc ions with magnesium dopants in the zinc oxide crystals, due to increase dopant concentration and the effect of aging and drying process [57]. Thus, the current study reveals that the temperature, time of drying process and the concentration dopant plays a significant role in the modification of crystal structure, thereby alters the morphology of the nanoparticles.

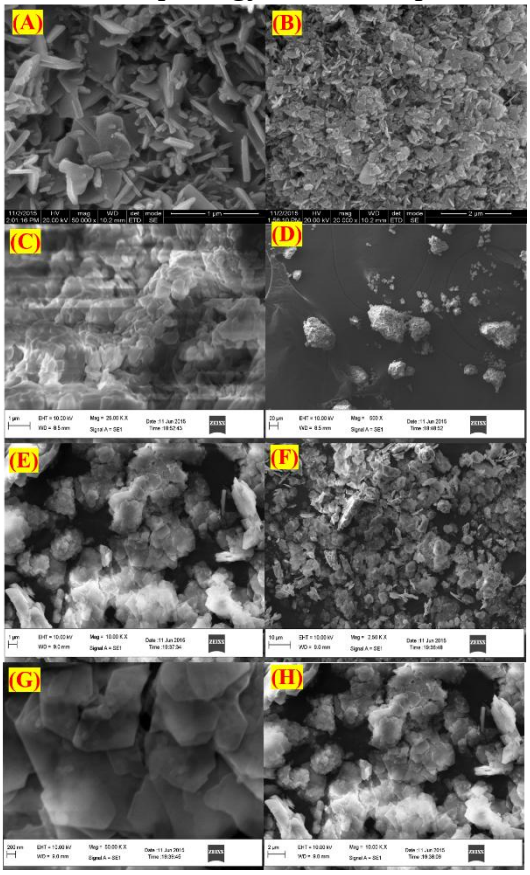

Figure 6. *Transmission electron micrograph of (A) pure ZnO (scale: 1µm), (B) pure ZnO (scale: 2µm), (C) Mg (0.1%) doped ZnO (scale: 1µm), (D) Mg (0.1%) doped ZnO (scale: 20µm), (E) Mg (0.2%) doped ZnO (scale: 1µm), (F) Mg (0.2%) doped ZnO (scale: 10µm), (G) Mg (0.3%) doped ZnO (scale: 200nm), (F) Mg (0.3%) doped ZnO (scale: 2µm).*

3.5. Photoluminescence Studies of Pure and Mg-doped ZnO

Figure 7 is the photoluminescence spectra of undoped and Mg-doped ZnO nanoparticles obtained from Horiba photoluminescence microspectrometer, MicOS iHR320 to analyse their photoluminescence properties at room temperature. The peaks at ~450, 490 and 540 nm were present in all the samples which showed the photoluminescence property of the nanoparticles. The peak at 450 nm is formed due to the strong near-band-edge emission and the presence of all the peaks in the visible spectrum region indicates that the sample exhibits photoluminescence only in the visible light region [58]. The peak at 490 and 540 nm is due to the superposition of green and yellow-orange emission bands. The increase in the peak intensity with respect to doping and increase in the dopant concentration indicates that the nanoparticle exhibits a blue shift [36]. Thus, these magnesium doped nanoparticles with green light emission ability can be highly useful in several biological applications due to their enhanced photoluminescence properties, especially for 0.3% of magnesium doped ZnO nanoparticles. The presence of more dopants in the ZnO nanocrystals creates interstitial position, reduces the band gap and helps in the enhanced green light emission.

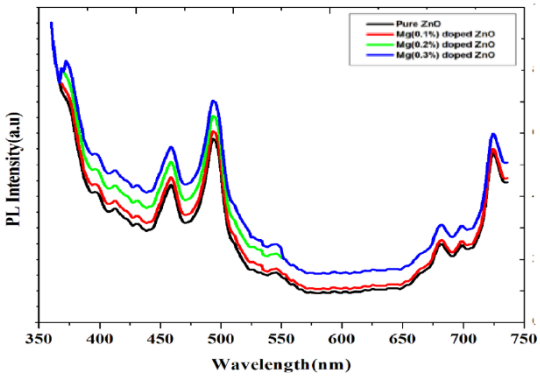

Figure 7. *PL spectra of sol-gel synthesized pure and Mg-doped ZnO*

The green light emitting Mg-doped ZnO nanoparticles are highly beneficial in biosensor applications. Huang et al. (2017) synthesized green light emitting aluminium doped zinc oxide nanowires via vapor transport for sensor applications [59]. Likewise, iron-nickel co-doped zinc oxide nanoparticles were synthesized as a scaffold for field effect transistor biosensors to electrochemically detect hexahydropyridine [60]. Moreover, ceria doped ZnO nanoflowers were used to fabricate luminol-based electrochemi-luminescence immunosensor for the detection of amyloid-β enzyme [61]. Thus, the enhanced green emission by Mg-doped ZnO nanoparticles fabricated in the present work will be beneficial in all these biosensor applications. Further, other Mg-doped ZnO nanoparticles will be beneficial as efficient sunlight-driven photocatalysts [28]. Since, Mg-doped zinc oxide nanoparticles possess several oxygen molecules, which is evident from the FTIR functional group analysis, these nano-particles will be highly beneficial as enhanced visible light-driven antibacterial agents [62]. Thus, the Mg-doped ZnO nanoparticles obtained via simple sol-gel procedure in the present work will be highly useful for biological applications which will be proved by extensive future research in this direction.

4. CONCLUSION

In Pure ZnO nanoparticles and 0.1-0.3% of magnesium doped ZnO nanoparticles were synthesized via simple sol-gel approach with commonly available zinc and magnesium precursors, ethanol as solvent and sodium hydroxide as reducing, capping and gelling agent. The samples were characterized via XRD, UV-visible spectrometer, FTIR, photoluminescence and TEM to study their properties. The result revealed that the magnesium doped ZnO nanoparticles possess enhanced photoluminescent property along with unique optical and structural properties. Thus, high percentage of green photoluminescent copper (0.3%) doped ZnO nanoparticles are proposed to be

useful in several bioimaging and biosensor applications from the results of the current study. Furthermore, other Mg-doped ZnO nanoparticle samples are also proposed to be beneficial for several biological applications. However, challenges such as larger size and polydispersity of the nanoparticles can be avoided and reduced by calcinating the sample at high temperature. Introduction of calcination in the sol-gel procedure will eventually enhance other properties along smaller and the monodispersed yield of nanoparticles.

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