ZnO-Mg Nanoparticles Produced by Pulsed Laser Ablation in Liquid (PLAL) Technique

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Abstract. Pulsed laser ablation in liquid (PLAL) technique has been used to synthesize ZnO and ZnO-Mg nanoparticles by conducting laser ablation of zinc target in pure water and Mg(NO3)2 solution. The absorbance spectra show redshifted peaks of ZnO with Mg inclusion indicating the lowering of the band-gap energy down to 3.09 and 3.01 eV from 3.28 eV of the pure ZnO. The higher frequency visible emission peaks of ZnO-Mg in the photoluminescence spectra indicate more recombination due to the formation of Mg interstitial state. The XRD measurement shows the diffraction of ZnO-Mg shifted into lower peak, resulting longer interplanar spacing, which matches to those obtained from HRTEM measurement.

1. Introduction

Nowadays, some of the metal oxides have been studied for their optical and structure properties, antimicrobial, and other important parameters [1,2]. Among the studied metal oxides, ZnO, MgO and CaO, are of particular interest because they are not only stable under harsh processing conditions, but also generally regarded as safe materials to human beings [3,4]. The safety factors of these materials show a great potential for antibacterial, medicine, food and biological application. Nano-hybrid materials structured by metal oxide nanoparticles (NPs) are known to be potential candidates for antibacterial, medicine and biological application [5-6]. The combination between ZnO and Mg nanostructure to form a hybrid structure was reported to improve structure and antimicrobial properties of ZnO alone [6].

Pulsed laser ablation in liquid (PLAL) is one reliable technique to produce metal, metal oxide and bi-phase metal/metal oxide nanostructures [7,8]. PLAL technique allows the absence of reductor and capping agent in the process and it is suitable for our purpose to prepared nanoparticles for antibacterial application, which requires a high purity and clean surface. Jimenez et al was able to produce nano alloy silica caped Au-Ag via PLAL technique, by focusing the laser beam on the surface Si target in Ag and Au ions solutions [7]. In this work the same technique was adapted to prepare ZnO-Mg nanostructure, where we believe it has not been conducted and explored before. The optical properties were measured using UV absorbance spectroscopy and photoluminescence spectroscopy (excitation 325 nm), while structure were observed using (transmission electron spectroscopy TEM) and X-ray diffraction (XRD).
2. Methodology

a. The ZnO-Mg nanostructures synthesis

The experiment was carried out by employing Nd:YAG laser as the light source of pulsed laser ablation in liquid (PLAL) with the wavelength and energy of 1064 nm and 100 mJ/pulse respectively. The pulse width and repetition rate were left default at 6 ns and 10 Hz. The experimental scheme can be seen in Figure 1. The laser ablation was performed by focusing laser beam on the surface of zinc plate (purity 99.5% purchased from Nilaco corp japan) in 5 mL (the height of the water from zinc target was 8 mm) pure water and Mg(NO$_3$)$_2$ solution resulting ZnO and ZnO-Mg colloidal suspension respectively. The ablation was taken place for 30 minutes. The concentration of Mg(NO$_3$)$_2$ solution was set 0.1 and 0.5 mM expecting different concentration of Mg on ZnO-Mg nanostructure. More details can be seen in Table 1.

![Figure 1. Schematic experimental setup of PLAL for ZnO and ZnO-Mg nanostructure synthesis](image)

| Sample name | Target | Solution          | Duration |
|-------------|--------|-------------------|----------|
| ZnO         | Zinc   | Pure water        | 30 minutes |
| ZnO-Mg 1    | Zinc   | Mg(NO$_3$)$_2$ 0.1 mM | 30 minutes |
| ZnO-Mg 2    | Zinc   | Mg(NO$_3$)$_2$ 0.5 mM | 30 minutes |

b. The optical characterization of ZnO-Mg nanostructures

The optical properties were studied using UV-Vis (UV-Visible) Spectrometer and PL 325 (Photoluminescence 325) spectrometer. The absorbance spectrum obtained from UV-Vis spectrometer further converted into tauc plot resulting predicted band gap value of the prepared ZnO and ZnO-Mg nanoparticles. The PL spectrum of ZnO, which consist of emission, and excitation of the sample was expected able to predict the occurrence of defect and impurities as an indication the Mg was formed in ZnO-Mg nanostructures. The PL samples were prepared by drying 1 ml colloid for ZnO and ZnO-Mg colloids on top of silicon wafer.

c. The structure characterization

XRD (X-Ray Diffraction) was used to study the phase formed and crystalline of ZnO and ZnO-Mg nanostructures, and TEM (Transmission Electron Microscopy) was used to observe the shape and size
of the prepared ZnO and ZnO-Mg nanostructures. For the XRD measurement, ZnO and ZnO-Mg colloidal suspension was dropped with the amount of 1 mL on the surface of silicon wafer and let it dry in the oven (30-40°C) for about 12 hours. The sample for TEM was prepared by dropping 100 μL of the colloids on the TEM grid and let it dry 12-24 hours.

3. Results and Discussion

a. The optical properties of ZnO-Mg nanostructures

The colloidal suspension of ZnO and ZnO-Mg nanoparticles synthesized by PLAL is presented in Figure 2. The colour of ZnO colloid nanoparticles was clear white. The usage of Mg(NO$_3$)$_2$ as the solvent has turned the colloid into more concentrated white, indicating not only ZnO, but also Mg has been formed in the colloid. Figure 3(a) shows the absorbance of ZnO nanoparticle and ZnO-Mg nanoparticle (ZnO-Mg 1 and ZnO-Mg 2). The absorbance peak of pure ZnO was found at the wavelength of 344.7 nm and the peak was red-shifted to 366.36 and 360.05 for ZnO-Mg 1 dan ZnO-Mg 2 respectively.

![Figure 2. Colloidal suspension of ZnO and ZnO-Mg nanoparticles prepared by PLAL technique](image)

The absorbance data was then converted into band-gap energy by following formula below [9]:

$$(\alpha \nu)^2 = A(\nu - E_g)$$

where, $A$ is a constant, $E_g$ is the optical bandgap, $\nu$ is Plank’s constant and $\alpha$ is the absorption coefficient. The plot of $(\alpha \nu)^2$ versus $E_g$ is presented in Figure 3(b). The spectrum converted into band-gap energy needs to be ensured that it was ZnO peak for the entire sample by using convolution feature. At some cases, especially for hybrid materials, an absorbance spectrum consists of several spectra including impurities occurred in the process. The band gap energy is lower with the higher concentration of Mg. The band optical gap energy measured for ZnO ZnO-Mg 1 and ZnO-Mg 2 in Table 2. The incorporation of Mg in the ZnO crystal affect the band gap structure of ZnO, hence it can reduce the bandgap energy of pure ZnO. This result is also experienced by some previous work [10], on applying Mg as a dopant of ZnO.
Figure 3. UV–Vis absorption spectra of ZnO and ZnO-Mg nanoparticles (a) and The band gap calculated by Tauc’s plot method for ZnO and ZnO-Mg nanoparticles

Table 2. Calculated optical band gap energy of ZnO and ZnO-Mg nanoparticles

| Sample name   | $E_g$ (eV) |
|---------------|------------|
| ZnO           | 3.28       |
| ZnO-Mg 1      | 3.09       |
| ZnO-Mg 2      | 3.01       |

The PL spectrum at the excitation wavelength of 325 nm is presented in Figure 4, which consist of two peaks for the entire measured sample. The first peak, named as UV emission peak, appears at 378.09 nm and the second peak, named visible emission lies at 575.46 nm. The UV and visible emission values correspond to photon energy of 3.26 eV and 2.19 eV. The first peak indicates the presence of ZnO, which appears due to the recombination of holes and electrons in the valence band and in the conduction band of ZnO. The second peak is, identified as deep level defect and impurities in ZnO nanoparticles. The visible emission peak for ZnO-Mg samples are much higher than the pure ZnO indicating more defect were formed. The formation Mg might also add shallow donor level in interstitial position ($Mg_i$), hence the increase of emission peak is suggested due to the occurrence of electron recombination in $Mg_i$ to valence band.
Figure 4. Photoluminescence spectra of ZnO and ZnO-Mg nanoparticles

b. The structure of ZnO-Mg nanostructures

The XRD result for ZnO and ZnO-Mg is presented in Figure 5a. The XRD pattern of the sample can was indexed as the hexagonal wurtzite structure. There are 6 peaks can be detected and there is no secondary phase measured within the detection limit for both ZnO and ZnO-Mg 2 nanoparticle sample. XRD of pure ZnO shows 31.79°, 34.52°, 36.24°, 47.73°, 56.55°, and 67.81° indexed as (100), (002), (101), (102), (110) and 103). There is no Mg or MgO peaks appeared in the spectrum, which suggesting dopant mechanism of Mg into host matrix. Other possibilities are the amorphous structure and the small amount of Mg such that the peak did not appear in the spectrum. The main peaks of wurtzite structure (100), (002), and (101)) are shown in Figure 5b, where peaks of ZnO-Mg1 are shifted into smaller angles in comparison to pure ZnO. This result is similar to a result obtained by Pradeev Raj et al, where it was due to the Mg2+ ions were well incorporated into host matrix/ZnO by substituting Zn2+ [10]. The smaller angle resulted from this process is an impact of difference radii of Mg2+ (0.57 Å) ions in comparison to Zn2+ ions (0.60 Å). Table 3 shows some characteristic of XRD measurement of ZnO and ZnO-Mg 2 samples, where 2θ is the peak position, hkl is the integers of the lattice plane, D is crystallite size (obtained via Scherrer Equation) and d is the interplanar spacing which also can be obtained by measuring lattice fringe on HRTEM of the sample.
Figure 5. XRD patterns of ZnO and ZnO-Mg 2 nanoparticles (a) and The main characteristic peaks ((100), (002), (101)) of ZnO wurtzite structure for ZnO and ZnO-Mg 2 nanoparticles.

Table 3. Calculated optical band gap energy of ZnO and ZnO-Mg nanoparticles

| Sample name   | Hkl | $2\theta$ (°) | D (nm) | d (nm) |
|---------------|-----|---------------|--------|--------|
| ZnO           | 100 | 31.86         | 13.1   | 0.281  |
|               | 002 | 34.52         | 14.7   | 0.260  |
|               | 101 | 36.35         | 15.3   | 0.247  |
| ZnO-Mg 2      | 100 | 31.76         | 17.8   | 0.282  |
|               | 002 | 34.45         | 21.6   | 0.260  |
|               | 101 | 36.24         | 17.7   | 0.248  |

The TEM and HRTEM (high resolution TEM) of ZnO and ZnO-Mg sample are presented in Figure 6a, 6b, 6c and 6d. The shape of nanoparticles is tending to be sphere to rod-like for both ZnO and ZnO-Mg.
Mg. There is no significant change of the size as the Mg was introduced in the pure ZnO structure. The size of nanoparticles is on the range of 20 – 100 nm with most of them have size of 50 nm. HRTEM measurement of ZnO and ZnO-Mg 2 shows different d-spacing or interplanar spacing. Pure ZnO has d-spacing of 0.281 and 0.259 nm corresponding to wurtzite of ZnO 100 and 002 respectively. The spacing of the interplanar tend to be larger for ZnO-Mg 2 than pure ZnO, 0.283, 0.261 and 0.247 nm which are corresponding to wurtzite of ZnO 100, 002 and 101. This result indicates Mg incorporated occupies the substitutional lattice, and the difference on ion radii of Zn in the host material and Mg causes local distortion of the crystal structure, hence the interplanar spacing has also changed.

4. Conclusion
ZnO and ZnO-Mg nanoparticles have been produced via PLAL technique by focusing Nd:YAG laser beam on the surface of zinc target in pure water and Mg(NO$_3$)$_2$ solution. The absorbance was measured using UV-Vis spectrometer. The resulting absorbance peak of of 344.7 nm for ZnO and the peak was red-shifted to 366.36 and 360.05 for ZnO-Mg 1 dan ZnO-Mg 2 respectively. This shows that the bandgap of ZnO-Mg decrease by the inclusion of Mg down to 3.01 eV for the highest concentration of Mg. The XRD peaks of ZnO-Mg 2 are shifted into smaller angles in comparison to pure ZnO which is
resulted as the smaller radius of Mg$^{2+}$ ions (0.57 Å) in comparison to Zn$^{2+}$ ions (0.60 Å). The same reason is responsible for larger spacing of the interplanar (d-spacing) with the inclusion of Mg in ZnO structure as shown by the results of XRD and HRTEM characterization.

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