CHAPTER - V

EFFECT OF CAPPING AGENTS ON THE SIZE AND MORPHOLOGY OF Zn_{1-x}Mg_xO NANOCRYSTALS

ABSTRACT

This chapter deals with the synthesis and characterization of Zn_{1-x}Mg_xO nanocrystals by low temperature sol-gel process. The effect of two different capping agents on the size and agglomerations of Zn_{1-x}Mg_xO was investigated. The structural properties of the material were investigated by X-ray diffraction analysis. The sample contains a single phase of ZnO with hexagonal wurtzite structure. The size and morphology of the synthesized materials was observed by FE-SEM and TEM analysis. The optical properties of the material were examined by UV-Vis absorption spectroscopy and photoluminescence studies. The cutoff wavelength was blue shifted due to quantum confinement effect from smaller size nanocrystals.
CHAPTER V

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5.1 Introduction

As we mentioned in chapter IV, the band gap of ZnO can be tuned by adding Mg and therefore Zn_{1-x}Mg_xO alloy is one of the promising material for novel functional properties [Chen et al., 2003; Minemoto et al., 2000; Schmidt et al., 2003]. The incorporation of Mg leads to low exciton binding energies in Zn_{1-x}Mg_xO compared to ZnO and it is useful for better charge transport in solar cell applications. Moreover, Zn_{1-x}Mg_xO has the same material advantages of ZnO due to its wide-band gap, less lattice mismatch with ZnO as the ionic radius of Mg^{2+} (0.57\AA) and Zn^{2+} (0.6\AA) are quite similar [Schmidt et al., 2003]. In addition, it was reported that the deep level emission was greatly enhanced in Zn_{1-x}Mg_xO with increasing Mg composition [Schmidt et al., 2003; Makino et al., 2000; Zhang et al., 2005; Gruber et al., 2004].

Recently, the nano ZnO is widely investigated as it has too many applications in optoelectronics, dye sensitized solar cells and bio related applications. Due to the above-mentioned advantages, the nano Zn_{1-x}Mg_xO material is also a promising material for the above applications. Moreover, the size and morphology of the nano materials plays a vital role in controlling the functional properties. The sol-gel based solution route is highly useful for preparing high quality metal oxide nano materials with relatively large area
growth. However, during the low temperature synthesis by sol-gel method, the nano materials are easily agglomerated due to high surface energy which leads to increases the number of grain boundaries and affect the quality of the nano material. In general, organic materials are used as capping agents to avoid the agglomeration and control the size of the growing nano material in the solution medium. Only very few works were reported on the preparation of Zn$_{1-x}$Mg$_x$O nanocrystals or thin films by low temperature solution routes like sol-gel process and wet chemical methods [Yang et al., 2009; Kim et al., 2009; Ghosh and Raychaudhuri, 2006; Xu et al., 2013]. Moreover, the effect of various capping agents on the size and morphology of Zn$_{1-x}$Mg$_x$O nanomaterial is not fully explored. Therefore, in this chapter, we attempted to study the effect of two different capping agents and their concentrations on the size and morphology of Zn$_{1-x}$Mg$_x$O (x=0.1) nanocrystals alloy. Moreover, the structural, morphological and optical properties of the synthesised material were investigated.

5.2 Synthesis of Zn$_{1-x}$Mg$_x$O nanocrystals with various capping agents

Nanocrystals of Zn$_{1-x}$Mg$_x$O with the composition of (x = 0.1) was synthesised by sol-gel process. Zinc acetate, Magnesium acetate and Sodium hydroxide (NaOH) were purchased from Aldrich and used as a source material to prepare the precursor solution without further purification. Two different capping agents such as TEA and TEABr were used as a capping agent to suppress the agglomeration of the nanocrystals. The appropriate amount of constituents such as Zinc acetate and Magnesium acetate were weighted and
added with de-ionised water under the stirring condition and 0.3 M of NaOH was added into the solution. Same kind of several precursor solutions were separately prepared under identical conditions. After that 0.2 M of TEA and TEABr were added into the precursor solutions prepared in three different containers before the formation of white precipitates to control the size of the crystals and the stirring was continued for the next five hours. In order to study the effect of concentration of capping agent, the precursor solution was prepared with three different concentrations of TEA such as 0.1, 0.2 and 0.5 M. In the present experiments, the value of x represents the initial mol percent of Magnesium acetate in the precursor solution. The precipitates were collected from the solution by centrifuge method and washed in ethanol before drying at 70 °C. Subsequently, the synthesised materials were annealed at 150 °C for two hours.

X-ray diffraction (XRD) of the synthesised samples was recorded using a Rigaku diffractometer with Cu Kα radiation. Morphologies of the prepared samples were observed by SEM, FE-SEM, and TEM annalysis. The composition of the constituents elements of the synthesised powders were analysed by Energy dispersive analysis by X-ray (EDX). The optical properties of the prepared nanocrystals were studied by optical absorption studies. The luminescence properties of the prepared materials were analysed photoluminescence studies.
5.3 Results and discussion

5.3.1 Structural analysis

Fig. 5.1 shows the XRD spectrum of the uncapped and 0.2M TEA capped Zn$_{1.3}$Mg$_x$O sample. The XRD pattern of the two samples are identical with pure ZnO (x=0) and thus the samples contain a single phase of ZnO with hexagonal wurtzite structure. Moreover, all the diffraction peaks were indexed and well matched with the standard JCPDS data [Schmidt et al., 2003].

From the results, it is obvious that the Mg ions are incorporated substitutionally in the ZnO lattice by replacing the Zn ions. Moreover, as the composition of Mg (x ≤ 0.1) is quite lower and within the limit of miscibility thereby MgO phase is not segregated in the present samples [Schmidt et al., 2003]. Further, the sharp and intense diffraction peaks illustrates the crystalline quality of the nanocrystals. The particle sizes of the nanocrystals were measured from the XRD spectrum using the Scherer’s equation (Eq.5.1).

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \quad (5.1) \]

Where, $\beta$ is the full width half maximum (FWHM) of a diffraction peak, $D$ is the particle size, $\lambda$ is the wavelength of X-rays (Cu K$\alpha$ = 0.1542 nm), $\theta$ is the Bragg diffraction angle. It was found that the calculated particle size of uncapped sample is 45 nm whereas the particle size is reduced to 38 nm for the 0.2 M TEA capped Zn$_{1.3}$Mg$_x$O sample. The calculated particle size of TEA capped Zn$_{1.3}$Mg$_x$O is well agreed with the size observed by TEM analysis (refer section 5.3.3).
Fig. 5.1: XRD spectra of uncapped and capped $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanocrystals.
5.3.2 Compositional analysis

The incorporation of Mg in ZnO and thereby the formation of \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) was confirmed by EDX analysis. Fig. 5.2 shows the EDX spectrum recorded for the 0.2 M TEA capped \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) nanocrystals. The peaks at 8.63 and 1 keV are caused by the Zn K\(\alpha\) and L\(\alpha\) radiations. The peak at 0.53 keV confirms the presence of O in the sample. Moreover, the weak peak at 1.25 keV confirms the presence of Mg in the \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) sample. Another peak at about 0.6 keV is due to carbon as the carbon tape was used to fix the samples for EDX analysis. No other peaks were observed in the spectrum which shows the purity of the synthesised material. Moreover, the obtained composition of \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) sample is shown in Table 5.1. From the table it is clear that the sample contain the Mg composition of 4.4 atomic %.

\[ \text{Table-5.1} \]

**Measured composition of \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) nanocrystals.**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Peak position (keV)</th>
<th>Weight percent</th>
<th>Atomic percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K(\alpha)</td>
<td>0.53</td>
<td>13.33</td>
<td>37.92</td>
</tr>
<tr>
<td>Mg K(\alpha)</td>
<td>1.25</td>
<td>1.47</td>
<td>2.74</td>
</tr>
<tr>
<td>Zn K(\alpha)</td>
<td>8.63</td>
<td>85.2</td>
<td>59.33</td>
</tr>
</tbody>
</table>
Fig. 5.2: EDX spectrum of Zn$_{1.3}$Mg$_3$O nanocrystals.
5.3.2 Morphological studies

Fig. 5.3 a and b shows the FE-SEM and TEM images of the 0.2 M TEA capped Zn$_{1-x}$Mg$_x$O (x = 0.1) nanocrystals. From the FE-SEM image it is clear that the synthesised materials are un-agglomerated with spherical morphology. The morphologies and size of the particles are clearly observed by TEM analysis as it is shown in Fig.5.3b. The sizes of the particles are around 40 nm with no agglomerations. From the results, it is clear that the TEA was effectively suppressed the agglomeration of the Zn$_{1-x}$Mg$_x$O nanocrystals. Fig. 5.4 a shows the FE-SEM image of 0.2M TEABr capped Zn$_{1-x}$Mg$_x$O (x = 0.1) nanocrystals. As can be seen from Fig. 5.4 a, the nanocrystals are obviously monodispersed with spherical like morphology. Fig. 5.4 b and c shows the TEM and HR-TEM images of TEABr capped Zn$_{1-x}$Mg$_x$O nanocrystals. From the TEM images it is clear that the nanocrystals are about 40-50 nm in size with triangular like morphologies. Moreover, the material is highly crystalline in nature as we can clearly see the lattice fringes in the HR-TEM images. In addition, unlike the case of ZnO, the clear change in morphology was not observed in TEA capped and TEABr capped Zn$_{1-x}$Mg$_x$O nanocrystals. This is probably due to the similarities of molecular structures of TEA and TEABr and thus they possibly have a similar kind of chemical interaction with Zn$_{1-x}$Mg$_x$O nanocrystal during the growth process.
Fig. 5.3a: FE-SEM image of 0.2 M TEA capped Zn$_{1.5}$Mg$_{0.5}$O nanocrystals.
Fig. 5.3b: TEM image of 0.2 M TEA capped Zn$_{1-x}$Mg$_x$O nanocrystals.
Fig. 5.4a: FE-SEM image of 0.2 M TEABr capped Zn$_{1.3}$Mg$_{0.7}$O nanocrystals.
Fig. 5.4b: TEM image of 0.2 M TEABr capped Zn$_{1-x}$Mg$_x$O nanocrystals.
Fig. 5.4c: HRTEM image of 0.2 M TEABr capped Zn_{1-x}Mg_{x}O nanocrystals.
Fig. 5.5 shows the FE-SEM image of 0.1 M TEA capped Zn$_{1-x}$Mg$_x$O nanocrystals. As we can see from the images, the materials are partly agglomerated with partly un agglomerated. Figure 5.6 a and b shows the FE-SEM and TEM images of 0.5 M TEA capped Zn$_{1-x}$Mg$_x$O nanocrystals. From these figures, it is clear that the materials are mono dispersed with no agglomerations. From the results, one can infer that the addition of 0.1 M of TEA is not enough to encapsulate all the growing nanocrystals and thus part of the nanocrystals are highly agglomerated. In the case of 0.5 M TEA added sample, the nanocrystals are completely un-agglomerated as evidenced from FE-SEM and TEM images. Moreover, the sizes and morphologies of the 0.5 M TEA added Zn$_{1-x}$Mg$_x$O nanocrystals are almost similar to that of 0.2 M TEA added Zn$_{1-x}$Mg$_x$O. Therefore, it is obvious that a critical quantity of capping agents is needed to fully encapsulate the growing nanocrystal, otherwise part of the materials may be agglomerated as we observed in the case of 0.1 M TEA added material. On the other hand, the addition of capping agents beyond the critical quantity will not affect or control the size and morphology of the nanomaterial. It is worth to note here that the critical quantity of the capping agents may be carried with every capping agent.
Fig. 5.5: FE-SEM image of 0.1 M TEA capped Zn$_{1.5}$Mg$_{0.5}$O nanocrystals.
Fig. 5.6a: FE-SEM image of 0.5 M TEA capped Zn$_{1.5}$Mg$_{0.5}$O nanocrystals.
Fig. 5.6b: TEM image of 0.5 M TEA capped Zn$_{1-x}$Mg$_x$O nanocrystals.
5.3.3 Optical absorption studies

The optical properties of the Zn$_{1-x}$Mg$_x$O nanocrystals were analyzed by UV-Visible optical absorption studies. Fig. 5.7 shows the optical absorption spectra of the uncapped and 0.2 M TEA capped Zn$_{1-x}$Mg$_x$O nanocrystals. In general, the cut off wavelength was observed at 380 nm corresponds to the band gap of 3.26 eV for bulk ZnO. In the present experiment, the absorption peak was observed at 368.5 nm for the uncapped Zn$_{1-x}$Mg$_x$O sample while it was blue shifted to 360 nm for the TEA capped Zn$_{1-x}$Mg$_x$O sample.

![Optical absorption spectra](image)

**Fig. 5.7:** Optical absorption spectra of uncapped and 0.2 M TEA capped Zn$_{1-x}$Mg$_x$O nanocrystals.
From the observed results, it is obvious that the synthesised nanocrystals has higher band gap than bulk crystal which should be due to edge related quantum confinement from the smaller size nanocrystals. The observed variation in the cut off wavelength of TEA capped Zn$_{1-x}$Mg$_x$O sample is due to effective size control by capping the growing nanocrystals.