Structural, Morphological and Optical Properties of Mg: ZnS Nanoparticle for Future Contribution in Different Biological Uses

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Abstract

The wet chemical co-precipitation technique has been used to prepare magnesium doped zinc sulfide nanocrystal powder at room temperature for future contribution in technological and biological applications. The crystal structural, morphology, optical properties, and the emission spectrum of the powder were characterized by x-ray diffraction (XRD), atomic force microscopy (AFM), UV-VIS spectrophotometer, and photoluminescence (PL) spectra. The analysis of XRD diffraction indicated that the powder had cubic zincblende structure and the calculated value of crystallite size was (15.9 nm) for the preferential orientation diffraction peak (111). The calculated energy gap of the Mg:ZnS nanoparticles was (3.87 eV) from absorbance spectrum. The PL spectrum of the nanoparticle confirmed two peaks located on (367 nm) and (485 nm).

Introduction

Semiconductor nanostructures researches attracted great significance in the latest years because of their optoelectronic properties and due to the high surface area to volume ratio and their properties of size related to quantum confinement, when the size of the material is in the nanoscale region, the carriers confine by the boundaries of the material [1].

The emission tenability of semiconductor nanocrystals makes them useful as chromospheres for several applications such as biological fluorescent markers, cell tracking, cell labeling, vivo imaging, and light-emitting diodes [2]. Since the structure size of this semiconductor becomes smaller, the energy gap increases as the energy levels become more alienated from each other and the density of states will be varied so these effects make this semiconductor properties differ from the bulk counterparts [3].

Zinc sulfide is an exciting II–VI semiconductor which has an important consideration at the latest decades because of its exciting properties, as the wide energy gap (3.7eV) at room temperature [4] and a broad optical transparency from (UV) to (IR) region. So, this optical transparency merged with thermal and chemical stability raises ZnS to be one of the majority materials which used for optical windows [1] and useful for technological applications of optoelectronic devices such as photovoltaic cells, electroluminescent devices and blue light emitting diodes [5-8].

Despite advantages of nanoparticles, the harmful effect has been thoroughly examined, it was revealed that it is mainly attributed to the toxic effects of metals leaching from the nanoparticles or derived from their intrinsic behavior such as the surface roughness and the size.

Moreover, the doping of these nanostructures with impurity ions can affect on the transition probabilities and electronic structure [9]. ZnS as it mention, is technologically better than other chalcogenides and chemically more stable, so it is regarded as a capable host material for the ions of transitional elements (e.g. Mn$^{2+}$ [10], Ni$^{2+}$ [11] and Cu$^{2+}$ [12]. ZnS nanostructures had been prepared by different methods, such as laser ablation [13], solvothermal [14], liquid template [15], sol–gel [16]. For more information and few researches that investigation the effect of magnesium Mg$^{2+}$ (alkaline earth metal) on ZnS nanostructure properties, the present work studied XRD, morphology, UV-VIS absorption, and PL spectrum of the Mg
doped ZnS nanoparticles prepared by the wet chemical co-precipitation technique.

**Experimental**

The wet chemical co-precipitation technique has been used to prepare Mg: ZnS nanocrystals at room temperature. Systematic reagent grade chemicals, zinc acetate (CH$_3$COO)$_2$Zn.2H$_2$O), magnesium chloride (MgCl$_2$), and sodium sulfide (Na$_2$S.H$_2$O) were used without extra decontamination. In separated flask, solutions of 0.1M sodium sulfide, 0.1 M zinc acetate, and 0.01M of magnesium chloride were prepared. In a standard synthesis, 5ml of zinc acetate (0.1M) was mixed with 3 ml of 0.01M Mg at room temperature. To this mixture, 10 ml of sodium sulfide was gradually added with stirring. With a centrifugation at 3000 rpm, the prepared powder was separated from the solution. Finally the ethanol was used to wash the sample.

X-ray diffraction with Cu Ka radiation (Rigaku Model, $\lambda = 1.5406$ Å) was used to confirm the crystalline structure and the size of the nanoparticles. The surface morphology photograph, surface roughness and morphological characteristics of the Mg: ZnS nanocrystallite powder were studied using (SPM model AA 3000 Angstrom Advanced Lns.,USA). The optical absorbance spectra for Mg:ZnS nanoparticles was measured by Hitachi F-2500 FL Spectro-photometer.

**Results and Discussion**

The XRD pattern of the Mg: ZnS nanopowder is shown in Figure 1. These patterns of the Mg:ZnS nanoparticles powder reveal three illustrious peaks corresponding to diffraction of the (111), (220), and (311) planes of the cubic phase of pure ZnS (JCPDS No 5-566) [18] at 2$\theta$ equals to 27.229 , 48.723, and 56.330 respectively. The figure illustrate that the structure of nanoparticles preferentially orientated along (111) directions and is similar to the pure ZnS but it becomes sharper and more intense when it doped with Mg. Any peaks of other impurities such as Zinc Oxide or other composites are not detected. The results of XRD patterns agree with other researches [4, 19]. The average size of nano-crystalline particle (D) was calculated using (FWHM), the full width at half maximum of the preferential diffraction peak (111), according to Scherrer formula [17,18]:

$$D = \frac{k \lambda}{B \cos \theta}$$  (1)

Where, $k$ is Scherrer constant (= 0.9), $\lambda$ is X-ray wavelength (=1.54056 Å), $B$ is FWHM of preferential diffraction peak (111) in radians, and $\theta$ is the angle of diffraction. The calculated value of average nano-crystalline size confirms that the prepared nanoparticle is in the regime of quantum confinement as shown in Table 1 which is closely value to that nano-grain size of Mg:ZnS nanoparticle prepared by another method [20]. The lattice constant of the preferential crystallite orientation (111) of nanoparticle was found from below formula [21] and tabulated in Table 1.

$$a = d \sqrt{h^2 + k^2 + l^2}$$  (2)

![Figure 1: The XRD pattern of the prepared Mg:ZnS nanoparticle](image)
One can observe from the table that the lattice constant, which is 5.380 Å is closely to the accounted value \( a = 5.406 \) Å [21].

Table 1: The parameters of XRD patterns and the calculated values of average nanocrystallite size \((D)\) and lattice constant \((a)\) of the preferential crystallite orientation (111) for the Mg:ZnS nanoparticle

<table>
<thead>
<tr>
<th>nanoparticle</th>
<th>( \beta \times 10^\circ ) (rad)</th>
<th>( 2\theta ) (degree)</th>
<th>( d ) (Å)</th>
<th>( D ) (nm)</th>
<th>( a ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg:ZnS</td>
<td>8.72</td>
<td>27.229</td>
<td>3.11</td>
<td>15.9</td>
<td>5.38</td>
</tr>
</tbody>
</table>

AFM images consider as the one of the efficient ways which using to study the material surface because of their high powerful analysis and resolution software [19]. AFM technique had been carried out for characterizing the morphologically of the prepared powder as shown in Figure 2. Two and three dimensional AFM images are illustrated in the figure. The images indicated the crystalline nature of the Mg:ZnS nanoparticle due to homogeneously distributed of the nanograins. The image (1482X1501nm) is employed for evaluating the root mean square roughness surface \( (R_q) \) and the average roughness \( (R_a) \) of the Mg:ZnS nanoparticle. All the AFM measurements \( R_a, R_q \) and the average grain size \( (D) \) were tabulated in Table 2.

![AFM images](image-url)

Figure 2: Two and three dimensional AFM images of the Mg:ZnS nanoparticle

The table indicated a low value of the surface roughness which is representing an important factor in photovoltaic application. Reducing in surface roughness value of the material improves the solar cells efficiency.

Table 2: The (AFM) measurements \( R_a, R_q \) and average grain size \((D)\) of Mg:ZnS nanoparticle

<table>
<thead>
<tr>
<th>nanoparticle</th>
<th>average roughness ((R_a, \text{nm}))</th>
<th>root mean square roughness surface ((R_q, \text{nm}))</th>
<th>average grain size ((D, \text{nm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg:ZnS</td>
<td>0.707</td>
<td>0.855</td>
<td>90.05</td>
</tr>
</tbody>
</table>

Synthesized Mg:ZnS nanoparticle’s optical properties are determined from absorbance spectrum in the range of (200-900 nm). UV–VIS absorbance spectrum of Mg doped ZnS a nanoparticle is depicted in Figure 3. The typical absorption edge at ultraviolet region lies in 320 nm, which shows that Mg:ZnS nanoparticle has blue shift. The excitons quantum confinement of the sample is causing this shift in the absorption edge, resultant in more distinct energy band of the individual nanoparticles. The host crystal size influences on the impurity quantum confinement. So, the confinement degrees and their effects increase as the host crystal sizes decrease [17]. By doping, Mg ions might be form new levels in the energy band of ZnS and caused the blue shift [22, 23]. The energy gap and the average size of Mg:ZnS nanoparticles have been calculated by equations 3 and 4 respectively. The absorption spectra and below formula were used to evaluate the energy gap of Mg:ZnS nanoparticles:

\[
E_{gn} = \frac{h \nu_{gn}}{hc/\lambda_{gn}} = \frac{hc}{\lambda_{gn}}
\]

Where \( E_{gn} \) is the energy gap in the optical spectra of the semiconductor nanoparticles and \( h \) is Planck’s constant. The value of nanoparticle energy gap was found to be 3.87 eV while the \( Eg \) for the bulk ZnS is 3.65 eV. This difference of energy gaps is due to the blue shifted in the edge of absorption spectrum. The effect of quantum confinement due to decreasing in the size of structures...
might be caused by increasing of the energy gaps of Mg:ZnS nanoparticles [23]. The size of particle (r) as a function of the wavelength of absorption peak (λp) for Mg:ZnS nanoparticle can be found by the following formula[24]. The calculated value was 8.95 nm.

\[
    r(\text{nm}) = \left[ \frac{0.2963 + (-40.1970 + 13620/\lambda_p)^{1/2}}{-7.34 + 2481.6/\lambda_p} \right]^2
\]  

(4)

Figure 3: UV–VIS absorbance spectra of Mg:ZnS nanoparticle

One of the most effective ways to study the optical, photochemical properties and electronic structure of semiconductor materials is photoluminescence spectrum, by which information like defects and surface oxygen vacancies, the transfer and trapping efficiency and immigration of charge carrier may be achieved [20]. Figure 4 shows the measured PL spectrum of Mg:ZnS nanoparticle at room temperature and shows the two peaks positioned are about 367 nm (3.37 eV) and 485 nm (2.55 eV). Usually two emission peaks can be observed for semiconductor nanocrystals. The first peak is called exaction which is sharp while the second peak is board and called trapped [25]. The emission peaks shown in the spectrum might be due to the emission of the gap. So, the strong emissions of band gap provide high-quality of crystalline nature of the prepared particles [26].

Figure 4: PL spectrum of Mg:ZnS nanoparticle

Conclusion

- Mg doped ZnS nanoparticle was effectively prepared by the wet chemical co-precipitation technique at room temperature. The prepared nanoparticle exhibits structure of cubic zincblende with high crystalline nature. According to Scherrer formula, the particle sizes average was found to be 15.9 nm.

- AFM images indicated crystalline nature of the Mg:ZnS nanoparticle due to homogeneously distributed of the nanograins.

- The absorption edge at UV region lies in 320 nm, which indicates that Mg:ZnS nanoparticle has blue shift.
The photoluminescence spectrum of Mg:ZnS nanoparticle was measured at room temperature.

References

