Influence of synthesis methods on various properties of Zinc oxide nanostructures

M. Sudha¹, Y.A. Syed Khadar², S. Surendhiran³, P. Manoj Kumar³, K.C. Suresh⁴, A. Balamurugan⁵*

1 Department of Physics, Government Arts College
Udhagamandalam – 643002, Tamilnadu, India

2 Department of Physics, K.S.R College of Arts and Science for Women
Tiruchengode -637215, Tamilnadu, India

3 Centre for Nano Science and Technology, K.S. Rangasamy College of Technology
Tiruchengode -637215, Tamilnadu, India

4 Department of Physics, Research and Development centre, Bharathiar University
Coimbatore – 641 046, India

5 Department of Physics, Government Arts and Science College
Avinashi – 641654, Tamilnadu, India

sudhaphd,gac@gmail.com¹, dryaskh@gmail.com², bala.snr@gmail.com⁵*

Abstract

In this research work, ZnO nanostructures have been synthesized using three different synthesis methods. The crystal nature and size, structural morphology and optical properties of the ZnO nanostructures differ according to the synthesis method employed. X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Particle size analysis (PSA) and UV-Visible spectroscopy (UV-Vis) studies were elaborately used to characterize physicochemical properties of ZnO nanostructures. Photocatalytic decolourisation of Rhodamine B dye under UV light irradiation was carried out using prepared ZnO nanostructures. Systematic comparative studies on various properties were made to know about the effects of synthesis method on properties of ZnO nanostructures.

Keywords: ZnO nanostructures; X-Ray Diffraction; FESEM
1. Introduction

Zinc oxide nanostructures are at the vanguard material of nano science research field due to their exclusive properties and extensive applications [1, 4]. The exploration on the preparation and properties of ZnO nanostructures has concerned a great agreement of attention, and a variety of methods have been hired to design and fabricate this kind of nanomaterial [5 - 7]. The transformation of bulk to nanoscale level has number of changes and enhancements towards efficiencies of physical and chemical properties of nanomaterials. The increase in surface area to volume ratio and also reduction of the particle size (in the vision of quantum confinement effects) are the two significant ones of these [8 -11]. The various synthesis methods and approaches used for the production of ZnO nanostructures. Every processing parameter such as synthesis methods, doping ions and concentration, calcinations temperature and medium are playing a vital role in chemical, physical and biological properties of nanomaterials [12 - 15]. Many attempts are made to prepare ZnO nanostructures by aforementioned processing parameters. In this present report, ZnO nanostructures were prepared by three different methods namely sol gel [16], sonication [17] and microwave method [18]. The effects of synthesis method on structural, physical and optical properties were studied using XRD, FESEM, and UV-Vis and PSA techniques.

Herein, ZnO nanostructures prepared by three different methods namely sol gel, sonication and microwave methods and characterized elaborately using XRD, FESEM, EDAX, UV-Vis, Particle size analysis. Finally we attempt to conclude a comprehensive comparative analysis on structural, optical and photocatalytic degradation efficiency of prepared ZnO nanostructures with earlier reports.

2. Experimental details

2.1 Materials and preparation of ZnO nanostructures

ZnO nanostructures were prepared by sol-gel, sonication and microwave method and Zinc acetate, sodium hydroxide and double distilled water (DD) were used as starting material without further purification. All the reagents were in analytical grade (AR) purity.

(i) Sol gel method: 1M of zinc acetate and 1M of sodium hydroxide was taken as starting material for ZnO nanostructures by this method. The desired amount of DD water was taken for Zinc acetate and mixed well with stirrer. After 15 mins; a transparent Zinc solution obtained, then the NaOH was slowly added to the zinc acetate solution by using burette till the pH of the solution reach to base value. After the pH value reached to 10 the solution containing beaker was allowed to dry in hot air oven for 12 hours. The dried samples was collected and grinded with pistol and mortar then the grinded powder was calcinated for 3 hours at 400° C. Hereafter this sample was termed as SG/ZnO.
(ii) **Sonication method:** An aqueous solution of Zinc acetate (1M, 100 mL) was kept in sonication chamber with 40Hz power of ultrasonic wave irradiation. The Sonicator equipment setting parameters were fixed for 5 sec of irradiation and 5 sec for rest; during the rest time, the NaOH (1M, 100 mL) solution was added to adjust the pH value. After the pH value reached to 10, the solution was allowed to dry and for calcination process at 400° C. Hereafter this sample was termed as SO/ZnO.

(iii) **Microwave method:** During this method of preparation, the same sol gel procedure for taken with addition of one step. After the Zinc acetate solution reaches the pH value of 10, and then the solution was transferred to Teflon beaker and kept in microwave oven for 30 mins with 300W power. After completion of drying and calcination process, sample was named as MW/ZnO.

### 2.2 Characterization of ZnO nanostructures

Characterization Techniques such as X-Ray Diffraction (XRD), UV-Visible spectroscopy (UV-Vis), FESEM-coupled with EDX, particle size analyzer (PSA) were used to characterize the prepared ZnO nanostructures.

To identify the structural identity and the average crystallite size of the prepared ZnO nanostructures was used by X-ray diffractometer (X’Pert PRO; PANalytical, the Netherlands). CuKa radiation (\( \lambda = 1.5406 \) Å) was used as a source to anaylyses the prepared ZnO nanostructures at the 2θ position from 10° to 80° with 20 step of 0.02°. The UV absorption spectra of ZnO nanostructures were recorded using UV–visible (UV–Vis) Spectrophotometer (Cary 8454; Agilent, Singapore) operated from the 180 – 800 nm spectral regions at a step size of 5 Å. The dispersed ZnO nanostructure (0.1 mg of ZnO nanostructures was dispersed in 5 ml double deionized water and sonicated for 3 minutes for uniform dispersion) was taken in a cuvette. The particle size distribution and average particle size of the ZnO nanostructures were carried out with a submicrometre particle size analyzer (Nanophox; Sympatec, Zellerfeld, Germany) using dynamic light-scattering (DLS) technique. Field Emission Scanning electron microscope (FE-SEM; JSM-6790 LS; JEOL, 40 Japan) was used to analyze the surface morphology of the prepared ZnO nanostructures.

**Photocatalytic degradation of Rhodamine B dye**

The photocatalytic degradation of Rhodamine B dye in the existence of ZnO nanoparticles below UV light irradiation was analysed as follows. Briefly, a 100 mg of prepared ZnO nanoparticles had been added into a 100 ml of aqueous Rhodamine B solution (50 mg/L) and stirred for 10 min to get clear suspension.
Then suitable quantity of the supernatant Rhodamine B answer used to be taken with 15 mins time interval to recognize the awareness of Rhodamine B the use of UV-Vis spectrophotometer by using absorption capability. Dye degradation effectively of ZnO nanoparticles below seen mild was once determined the usage of the under relation.

\[
\text{Dye degradation efficiency } \eta = \left(1 - \frac{C}{C_0}\right)
\]

Dye degradation efficiency where \(C\) and \(C_0\) are final and initial concentration of Rhodamine B dye solution.

3. Results and interpretations

The X-ray diffraction patterns of ZnO nanostructures prepared by sol-gel, sonication and microwave methods, correspondingly shown in Figure 1 (a, b and c). The XRD patterns for all the prepared ZnO nanostructures were recorded at room temperature. The recorded diffraction peaks of ZnO nanostructures were indexed to a hexagonal wurtzite structure and were in consistent agreement with standard JCPDS card no. 36-1451 with space group of P63mc. No other diffraction peaks were recorded in XRD pattern which indicates the absence of impurities, destruction of by-products due to the calcination at 400°C. The observed broaden peak at 31.7°, 36.2° and 56.3° indicates the formation of ZnO. There is no major variation in diffraction peak for all samples but the relative intensities of the peaks are gradually increased which directly portrays the formation of ZnO and greatly enhance crystallization. The effect of microwave irradiation is main cause to high level formation of ZnO nanostructures compared with other two synthesis methods [19]. The MW/ZnO sample has high intensity peaks in diffraction pattern without any further small peak whereas observed in SG/ZnO and SO/ZnO samples.
Figure 1 XRD patterns of ZnO nanostructures synthesized by sol-gel (a), sonication (b) and microwave methods (c).

The average crystalline size of the prepared ZnO nanostructures were calculated using Scherrer’s formula [20]:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where D is average crystallite size, K is a constant of 0.9, λ is the X-ray wavelength (0.15406 nm), β is the full width at half-intensity maximum of XRD peak and θ is the diffraction angle.

The crystalline size of the ZnO nanostructures is calculated to be 44, 41.7 and 39.2 nm respectively for SG/ZnO, SO/ZnO and MW/ZnO nanostructures. Among the methods used to synthesis ZnO nanostructures, the microwave irradiation method strongly plays a role in formation and crystallization of ZnO with lower crystal size compared with sol-gel and sonication method [21].
Figure 2: M images and EDAX pattern of ZnO nanostructures synthesized by sol-gel (a i & ii), sonication (b i & ii) and microwave (c i & ii) methods

The surface morphology of the SG/ZnO, SO/ZnO and MW/ZnO nanostructures were revealed in figure 2 (a, b and c) and it was captured by FESEM with EDAX setup. Figure 2a shows spherical like morphology with agglomeration for SG/ZnO; Figure 2b depicts hexagonal crystal morphology with the 20 nm length and also with uniform distributions. Figure 2c shows MW/ ZnO morphology that were in rod like structure bunches with 3 – 8 nm thickness and 17 – 22 nm length scale levels.
This FESEM results shows the sonication and microwave irradiation majorly cause for the formation of different type of morphology ZnO nanostructures [22]. The EDAX result clearly shows that there are no unwanted impurities presents. All the prepared ZnO nanostructures were high in purity and proper crystal formation which was already conformed in XRD results [23]. By this FESEM results, it is comes to know clearly the synthesis method mainly cause for formation of different morphology and also with purity. The elemental composition of the prepared ZnO nanostructures obtained from EDX were given in table 1.

The average particle size of the prepared ZnO nanostructures were ranges around 60 nm to 70 nm and exact values of average particle size is given in figure 3 (a, b and c respectively for SG/ZnO, SO/ZnO and MW/ZnO nanostructures. Since the size of the nanoparticles is most important ruling property for optical and electrical properties of the nanoparticle, similarly for all other applications according to quantum confinement effect [24]. The average particle size distribution of SG/ZnO, SO/ZnO and MW/ZnO nanostructure are 69.1, 66.3 and 63.7 nm respectively. The sizes of the nanoparticles are gradually reduced according to its opted synthesis method. The above results clearly indicate that the synthesis method of the nanoparticle play a dominant role in size of the preparing nanoparticle [25].

The UV-Vis spectrum of SG/ZnO, SO/ZnO and MW/ZnO nanostructures is shown in figure 4 (i). The band edge absorption of prepared nanostructures was observed at 372, 374 and 375 nm for SG/ZnO, SO/ZnO and MW/ZnO nanostructures correspondingly. The energy bandgap of the prepared ZnO nanostructures according to wavelength absorption edge basis and they are 3.341, 3.323 and 3.315 eV for SG/ZnO, SO/ZnO and MW/ZnO nanostructures respectively [26].The direct energy bandgap energy values of prepared nanostructures were obtained using standard derivatives of photon energy and absorbance value were shown in figure 4 (ii) also known as Tauc plot. The determined bandgap energy values of SG/ZnO, SO/ZnO and MW/ZnO nanostructures were 3.46, 3.41 and 3.39 eV. From the above given results, it is comes to know that ZnO nanostructures are highly semiconducting material and can be easily modify their optical properties and bandgap values by the influence of synthesis methods [7-8]. The comparative assessment made on the results obtained from XRD, DLS and UV was shown in table 2.
Table 1. Elemental composition of ZnO nanostructures

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SG/ZnO</td>
</tr>
<tr>
<td>O K</td>
<td>36.66</td>
</tr>
<tr>
<td>Zn K</td>
<td>63.34</td>
</tr>
</tbody>
</table>

Figure 3 Particle size distribution curves of ZnO nanostructures by sol-gel (a), sonication (b) and microwave (c) methods
Table 2. The results from XRD, DLS and UV-Vis of SG/ZnO, SO/ZnO and MW/ZnO nanostructures

<table>
<thead>
<tr>
<th>S. No</th>
<th>Sample</th>
<th>Crystalline size (nm) from XRD</th>
<th>Particle size (nm) from DLS</th>
<th>UV peak ($\lambda_{max}$)</th>
<th>Band gap (eV) by $\lambda_{max}$</th>
<th>Band gap (eV) by Tauc plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>SG/ZnO</td>
<td>44</td>
<td>69.1</td>
<td>372</td>
<td>3.341</td>
<td>3.46</td>
</tr>
<tr>
<td>2.</td>
<td>SO/ZnO</td>
<td>41.7</td>
<td>66.3</td>
<td>374</td>
<td>3.323</td>
<td>3.41</td>
</tr>
<tr>
<td>3.</td>
<td>MW/ZnO</td>
<td>39.2</td>
<td>63.7</td>
<td>375</td>
<td>3.315</td>
<td>3.39</td>
</tr>
</tbody>
</table>

Rhodamine B is one of basically used dyes in the textile industries therefore it is substantially studied as a traditional water pollutant. The degradation of Rhodamine B in the presence of prepared ZnO nanoparticles below mild irradiation used to be studied for the period of 120 mins.
Figure 5. Photocatalytic activity of ZnO nanostructures towards Rhodamine B dye

Fig. 5 (a) (b) and (c) suggests the time structured UV-Vis absorption spectrum of Rhodamine B dye in presence of SO/ZnO, SG/ZnO and MW/ZnO nanoparticles, respectively under the UV mild irradiation. It is noted that UV absorption of Rhodamine B dye at 554 nm falls shortly with growing period which revealed that SO/ZnO, SG/ZnO and MW/ZnO nanoparticles can easily oxidize the Rhodamine B underneath UV light illumination. Moreover, it is certainly suggests that the photocatalytic undertaking of MW/ZnO is substantially greater than that SO/ZnO and SG/ZnO nanoparticles. The photocatalytic degradation efficiency of SO/ZnO, SG/ZnO and MW/ZnO nanoparticles for the length of ninety mins on Rhodamine B dye degradation are 92.1, 93.7 and 96.5 %, respectively.
The formation of OH and O$_2$ depends upon the light absorption potential of organized ZnO nanoparticles. The consequences bought from UV-Vis studies evidently indicate that SO/ZnO, SG/ZnO and MW/ZnO nanoparticles has notable capability toward photon absorption in ultraviolet and seen location of electromagnetic spectrum. Hence the splendid band shape of photocatalytic materials is very essential for better generation of radicals (OH) and superoxide radicals (O$_2$). When the prepared ZnO photocatalyst was irradiated with photon having energy higher than band gap, the valance band electrons will receives excited and it can be transferred to the conduction band by means of leaving the identical number holes in the valance band. As a result, electrons in conduction band and holes in valence band can react with water molecules and dissolved oxygen and it can generate hydroxyl radicals (OH) and superoxide radicals (O$_2$). These lively species can without problems break down Rhodamine B dye molecules into H$_2$O, CO$_2$ and other forms [27, 28].

4. Conclusion

ZnO nanostructures (SG/ZnO, SO/ZnO and MW/ZnO) were prepared by three different methods and characterized elaborately. The ZnO nanostructures had a hexagonal wurtzite structure. The range of average crystalline sizes was decreased from 44 to 39 nm according to its preparation method. Three different types of morphology were detected from FESEM analysis; agglomerated spherical morphology, hexagonal structure and rod like morphologies respectively for SG/ZnO, SO/ZnO and MW/ZnO nanostructures. A strong evident obtained from UV-Vis spectrum that the band gap energy can be modify by changing the synthesis methods of nanoparticles. Herein the energy bandgap values of SG/ZnO, SO/ZnO and MW/ZnO nanostructures were decreased from 3.341 to 3.315 eV. By the overall observations from above obtained results of SG/ZnO, SO/ZnO and MW/ZnO nanostructures, the synthesis method plays a foremost key role in structural morphology, optical property, purity and also in crystalline nature and they may be used for multi-functional applications such as optical and microwave applications, biological applications and energy applications.

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