Synthesis and Characterization of ZNO/MN Nanocomposite by using Sol-Gel Method

S K W Ningsih*, B Bahrizal, E Nasra, U K Nizar, R Farisya

Chemistry Department, Faculty of Mathematics and Science, Universitas Negeri Padang, Jl. Prof. Hamka, Air Tawar, Padang 25131, Indonesia

*sherly14@fmipa.unp.ac.id

Abstract

Zink oxide doped Mn nanocomposites were synthesized by simple sol-gel method at low temperature by using combination of aquadest with methanol as the solvent and ethylene glycol as the additive. Zink acetate dehydrate and manganese chloride tetrahydrate were used as the precursors. Composition dopants were 1,3,5, and 7%. The crystals were formed by drying at 110°C for 1 hour, after which they were heated at ±500°C for 2 hours. The as-prepared ZnO/Mn nanocomposites were characterized by X-ray diffraction (XRD) and UV Diffuse Reflectance Spectrometer (UVDRS). The XRD patterns of the ZnO nanocrystals showed that they are mostly hexagonal wurtzite with specific peaks at 2θ = 31, 34, 36, 47, 56, 63, 66 dan 69. The sizes of the ZnO doped Mn particles produced with 1%, 3%, 5%, and 7% were 18-95; 17-87; 18-96; 19-98 nm, respectively. UVDRS analysis showed that the band gap of the ZnO were 2.60; 2.90; 2.99 dan 3.01 eV for 1%, 3%, 5%, and 7% Mn respectively.

1. Introduction

Nanoparticles are particles measuring between 1-100 nanometers[1]. These particles are part of nanotechnology that is very popular and growing rapidly since early 2000[2]. Nano-sized materials have been applied in various fields as catalysts, coatings, semiconductors, pharmaceutical and electronic products[3].

One of the most widely synthesized materials into nanoparticles is Zinc Oxide (ZnO). ZnO exhibits exciting optical, acoustic and electrical properties that have a number of potential applications in the fields of electronics, optoelectronics and sensors. In addition, ZnO has several advantages including a stable chemical structure, non-toxic, and can be used as an additive into various materials, and availability in nature is very abundant so that the price is cheap[4].

Zinc Oxide (ZnO) is an important semiconductor material because it has a wide band gap, so it is widely used for applications such as transparent conductors, solar cell windows, gas sensors, photovoltaic devices[5] and photocatalysts[6]. The semiconductor material is a good photocatalyst for the degradation of pollutants as well as toxic compounds namely Zinc Oxide (ZnO), Titania (TiO2), Tungsten Oxide (WO3), Zinc Stannate (Zn2SnO4)[7]. ZnO has a relatively large size and a small surface area.

The process of forming a nanomaterial will affect the properties of the material itself, in addition additive addition will also modify its properties. Additives are additives used to control yield morphology. With the addition of these additives, materials obtained that have microstructural homogenisity and small particle size are generated so that material reactivity increases[8].

Doping is an effective method for changing physical properties (e.g. optical, magnetic and electrical properties) in materials and will extend their application to the material from its basic
properties[9]. Doping with 3d metals such as Mn, Ni, Fe, Co, Cr and the like will increase the surface area and reduce the particle size of ZnO nanoparticles. In this study, ZnO nanoparticles doped with Mn2+ (Manganese). Various studies have shown that Mn doped semiconductors have affected the physical, chemical and structural properties of pure ZnO nanoparticles. For example, the optical properties of pure ZnO nanoparticles especially on band gap tunings can be greatly increased at the nanoscale with doped Mn.

There are several parameters that will surely affect the particle size, shape and optical properties of ZnO doped Mn nanoparticles such as the effect of dopant ion concentration of manganese, pH and surfactant[10]. In this study only focused on the effect of dopant Mn concentration with percent weight per volume (w / w) of 1%, 3%, 5% and 7%.

This manganese metal is usually not used in a pure state but as a mixture. Manganese is metallic with a melting point of about 1244 °C and a boiling point of 1962 °C. In pure state, manganese metal is hard, breakable, and silver-white. Manganese is easily oxidized by air, reacts slowly with water, and forms various compounds with varying degrees of oxidation from +2 to +7. In this study, other materials of relatively cheap price such as MnCl2.4H2O are found.

Attempts to synthesize nano ZnO have been widely practiced. Some of the most commonly used methods are Co-Precipitation[11], solvothermal[12], wet-chemical[13]. These methods have advantages and disadvantages of each. One other method that has been developed is the sol-gel method. Sol gel technique is more commonly used in nanoparticle synthesis because it has several advantages as follows: based on the product produced by sol-gel process obtained better homogeneity. High purity and fast crystallinity formation process[14]. Based on the energy used, the sol-gel technique is quite economical[15]as it can take place at low temperatures. Because the reaction takes place at low temperatures, the separation phase and the process of rapid crystal formation hence in terms of operational costs on the sol-gel process is quite economical. In terms of environmental process sol-gel including environmentally friendly[16]because the waste generated is quite low[17].

Zinc oxide (ZnO) is one of the popular semiconductor that have a wide band gap of 3.37 eV with large exciton binding energy of 60 meV. ZnO have extensive application due to its electrical and optical properties. ZnO can be applied in many applications, including gas sensors, generators, field emission transistors, ultraviolet photodetectors, in biomedical systems, biosensors, electronic materials, light emitting diode, solar cellsand piezoelectric transducer.

There are several ways to produce ZnO nanoparticles such as thermal decomposition, carbothermal reduction process, solid sate method, hydrothermal process, sonochemical methods, chemical vapor deposition (CVD), metal organic chemical vapor deposition (MO-CVD), polymerization method, precipitation process, and sol-gel method. Sol-gel process is one of the simplest and lowest cost (inexpensive).

Here, the synthesized ZnO doped Mn nanoparticles prepared by sol-gel method. Zinc acetate dihydrate was used as precursor, combination of aquades and methanol was used as solvent, and ethylene glicol as the additives. The various compositions were used 1, 3, 5 and 7%. Sol-gel method has a number of advantages over other methods such as inexpensive equipment, will produce small particle size and uniform distribution particle with highest homogenity[8].

2. Material
All the reagents were analytical reagent grade and were used without further purification. The precursors used in this research were zinc acetate hydrate[Zn(CH3COO)2.2H2O] (Merck) and manganese chloride tetrahydrate[MnCl2.4H2O] (Merck). Combination of aquades and methanol was used as the solvent and ethylene glicol was used the additive.

3. Synthesis of ZnO nanoparticles
A total of 2.744 g Zn(CH3COO)2.2H2O was dissolved with 50 mL of aquades and methanol mixture with a ratio of 1: 4 in a 50 mL beaker. Closed with aluminum foil paper and stirred using a magnetic stirrer for 40 minutes. In the solution was added manganese chloridatetrahydrathidrat[MnCl2.4H2O] as dopan with 1% concentration and distirer for 40 min. Mixed the positive is 1.4 mL of ethylene glicol and stirred for 90 minutes. The solution is allowed for one night. The second solution is made by adding 3%, 5% and 7% dopants in the same way. The soles obtained after stirring are then dried in the
oven at 110 °C for 1 hour. The results obtained are included in the furnace at a temperature of 500°C for 2 hours. The samples obtained are then crushed using mortar and pestle. Finally, the dried powder was ground in agate mortar. The synthesized ZnO nanoparticles were analyzed by using X-ray Diffraction (XRD) with a diffractometer by using monochromatic CuKα with λ = 1.5406 and band gap study was carried out by Ultra Violet Diffuse Reflectance Spectrometer (UVDRS).

4. Results and discussion

4.1. Sol ZnO doped Mn with various composition preparations

| Composition of ZnO doped Mn | Observations |
|----------------------------|--------------|
| 1% Zinc acetate dihydrate easily dissolved in the solvent mixture produces a clear solution, after addition of manganese chloride tetrahydrate 1% yields clear color of solution, continued with ethylene glycol is added the color of the solution becomes clear. |
| 3% Zinc acetate dihydrate easily dissolved in the solvent mixture produces a clear solution, after addition of manganese chloride tetrahydrate 3% yields clear color of solution, continued with ethylene glycol is added the color of the solution becomes clear. |
| 5% Zinc acetate dihydrate easily dissolved in the solvent mixture produces a clear solution, after addition of manganese chloride tetrahydrate 5% yields clear color of solution, continued with ethylene glycol is added the color of the solution becomes clear. |
| 7% Zinc acetate dihydrate easily dissolved in the solvent mixture produces a clear solution, after addition of manganese chloride tetrahydrate 7% yields clear color of solution, continued with ethylene glycol is added the color of the solution becomes clear. |

Characterization of ZnO nanoparticles, XRD patterns

![Figure 1. XRD pattern of ZnO doped Mn 1% nanoparticle synthesized by using ethylene glycol as additive](image)

The X-ray diffraction pattern of the ZnO synthesized by using ethylene glycol as additive was shown in Fig.1. This data clearly shows distinct peaks at 2θ = 31.72; 34.38; 36.19; 47.48; 56.67;
62.84; 67.87 and 69.07. The peaks have been identified as peaks of hexagonal ZnO (wurtzite) crystallites with various diffracting planes [100], [002], [101], [102], [110], [103], [112] and [201], respectively. ZnO nanoparticle posses a high crystallinity since all the peaks was very sharp. All of the reflections in this pattern can be readily indexed to a hexagonal phase of ZnO which is in good agreement with the literature result(ICCD No. 01-080-0075). The average crystalline size of the synthesized ZnO doped 1% Mn nanoparticle prepared by using ethylene glycol as additive was calculated by using Scherrer to be about 32.15- 95.37 nm (Table 2).

### Table 2. XRD data of ZnO doped Mn 1% nanoparticle prepared by using ethylene glycol as additive

| Pos.[^2Th.| | Height | FWHML | d-spacing | Rel. Int. | Crystallite size (nm) |
|---|---|---|---|---|---|---|
| 31.7229 | 3929.51 | 0.2047 | 2.82072 | 58.66 | 39.90 |
| 34.3811 | 2787.33 | 0.2558 | 2.60848 | 41.61 | 32.15 |
| 36.1984 | 6698.23 | 0.2303 | 2.48158 | 100.00 | 32.31 |
| 47.4852 | 1465.44 | 0.2184 | 1.91476 | 21.88 | 37.27 |
| 56.6755 | 2382.91 | 0.0936 | 1.62685 | 27.77 | 95.37 |
| 62.8493 | 1911.73 | 0.2808 | 1.47743 | 28.54 | 32.79 |
| 67.8753 | 1633.39 | 0.1872 | 1.37975 | 24.39 | 50.59 |
| 69.0721 | 810.16 | 0.1872 | 1.35873 | 12.10 | 50.95 |

**Figure 2.** XRD pattern of ZnO doped Mn 3% nanoparticle synthesized by using ethylene glycol as additive

The X-ray diffraction pattern of the ZnO doped 3% Mn synthesized by using ethylene glycol as additive was shown in Fig.2. This data clearly shows distinct peaks at 2θ = 31.71; 34.37; 36.18; 47.48; 56.54; 62.79; 67.88 and 69.03. The peaks have been identified as peaks of hexagonal ZnO (wurtzite) crystallites with various diffracting planes [100], [002], [101], [102], [110], [103], [112] and [201], respectively. ZnO nanoparticle posses a high crystallinity since all the peaks was very sharp. All of the reflections in this pattern can be readily indexed to a hexagonal phase of ZnO which is in good agreement with the literature result(ICCD No. 01-079-0207). The average crystalline size of the synthesized ZnO doped 3% Mn nanoparticle prepared by using ethylene glycol as additive was calculated by using Scherrer to be about 35.47-87.20 nm (Table 3).
Table 3. XRD data of ZnO doped Mn 3% nanoparticle prepared by using ethylene glycol as additive

| Pos. [°2Th.] | Height [cts] | FWHMLeft [°2Th.] | d-spacing [Å] | Rel. Int. [%] | Crystallite size (nm) |
|--------------|--------------|------------------|---------------|--------------|----------------------|
| 31.7126      | 2570.15      | 0.2303           | 2.82161       | 53.36        | 35.47                |
| 34.3740      | 2081.06      | 0.1535           | 2.60900       | 43.20        | 43.58                |
| 36.1846      | 4816.87      | 0.2047           | 2.48250       | 100.00       | 40.38                |
| 47.4844      | 1163.64      | 0.1791           | 1.91479       | 24.16        | 47.93                |
| 56.5411      | 1840.70      | 0.1023           | 1.62770       | 38.21        | 87.20                |
| 62.7995      | 1439.20      | 0.1535           | 1.47971       | 29.88        | 59.97                |
| 67.8886      | 1214.39      | 0.1535           | 1.38065       | 25.21        | 61.70                |
| 69.0344      | 651.42       | 0.2558           | 1.36051       | 13.52        | 37.28                |

Figure 3. XRD pattern of ZnO doped Mn 5% nanoparticle synthesized by using ethylene glycol as additive

The X-ray diffraction pattern of the ZnO doped 5% Mn synthesized by using ethylene glycol as additive was shown in Fig.3. This data clearly shows distinct peaks at 2θ = 31.72; 34.40; 36.17; 47.48; 56.53; 62.77; 67.90 and 69.01. The peaks have been identified as peaks of hexagonal ZnO (wurtzite) crystallites with various diffracting planes [100], [002], [101], [102], [110], [103], [112] and [201], respectively. ZnO nanoparticle possesses a high crystallinity since all the peaks was very sharp. All of the reflections in this pattern can be readily indexed to a hexagonal phase of ZnO which is in good agreement with the literature result (ICCD No. 01-080-0074). The average crystalline size of the synthesized ZnO doped 5% Mn nanoparticle prepared by using ethylene glycol as additive was calculated by using Scherrer to be about 40.18-101.20 nm (Table 4).

Table 4. XRD data of ZnO doped Mn 5% nanoparticle prepared by using ethylene glycol as additive

| Pos. [°2Th.] | Height [cts] | FWHMLeft [°2Th.] | d-spacing [Å] | Rel. Int. [%] | Crystallite size (nm) |
|--------------|--------------|------------------|---------------|--------------|----------------------|
| 31.7263      | 2275.97      | 0.1791           | 2.82043       | 55.80        | 45.61                |
| 34.4053      | 2626.48      | 0.2047           | 2.60670       | 64.40        | 40.18                |
| 36.1766      | 4078.59      | 0.1791           | 1.91485       | 23.85        | 41.93                |
| 47.4828      | 972.56       | 0.2047           | 1.62789       | 29.78        | 58.12                |
| 56.5341      | 1214.47      | 0.1535           | 1.47971       | 29.88        | 59.97                |
| 62.7771      | 1350.67      | 0.1791           | 1.38065       | 25.21        | 61.70                |
| 67.9081      | 404.11       | 0.2047           | 1.36051       | 13.52        | 37.28                |
| 69.0110      | 922.63       | 0.0936           | 1.37916       | 22.62        | 101.20               |
The X-ray diffraction pattern of the ZnO doped 7% Mn synthesized by using ethylene glycol as additive was shown in Fig. 4. This data clearly shows distinct peaks at 2θ = 31.70; 34.37; 36.18; 47.45; 56.51; 62.78 and 67.87. The peaks have been identified as peaks of hexagonal ZnO (wurtzite) crystallites with various diffracting planes [100], [002], [101], [102], [110], [103], [112] and [201], respectively. ZnO nanoparticle possesses a high crystallinity since all the peaks was very sharp. All of the reflections in this pattern can be readily indexed to a hexagonal phase of ZnO which is in good agreement with the literature result (ICCD No. 01-076-0704). The average crystalline size of the synthesized ZnO doped 7% Mn nanoparticle prepared by using ethylene glycol as additive was calculated by using Scherrer to be about 40.18-101.85 nm (Table 5).

**Table 5.** XRD data of ZnO doped Mn 7% nanoparticle prepared by using ethylene glycol as additive

| Pos.[°2Th.] | Height [cts] | FWHM[°2Th.] | d-spacing [Å] | Rel. Int. [%] | Crystalite size (nm) |
|-------------|-------------|-------------|---------------|--------------|----------------------|
| 31.7017     | 3504.03     | 0.1791      | 2.82256       | 54.78        | 45.60                |
| 34.3701     | 3013.57     | 0.2047      | 2.60929       | 47.11        | 40.18                |
| 36.1802     | 6396.43     | 0.1535      | 2.48279       | 100.00       | 46.15                |
| 47.4540     | 1312.93     | 0.1535      | 1.91595       | 20.53        | 55.91                |
| 56.5164     | 2018.06     | 0.1791      | 1.62835       | 31.55        | 49.80                |
| 62.7865     | 1750.14     | 0.1279      | 1.47998       | 27.36        | 71.97                |
| 67.8713     | 1302.54     | 0.1535      | 1.38096       | 20.36        | 61.69                |
| 68.9944     | 677.51      | 0.0936      | 1.36007       | 10.59        | 101.85               |
Figure 5 depicts the band gap data of ZnO doped Mn. The effect of various compositions were studied in order to obtain the band gap values of ZnO. The synthesized ZnO doped Mn nanoparticles prepared by using 1, 3, 5 and 7% dopant composition were 2.60, 2.90, 2.99 and 3.01 respectively. The composition dopant of 1% Mn has been the smallest band gap energy data.

5. Conclusion
ZnO doped Mn nanocomposites were successfully prepared by sol-gel method with various composition of dopants. The additives play a significant role on the crystalline size and morphology of the ZnO nanoparticles. XRD data for ZnO doped 1, 3, 5, 7% Mn prepared by using ethylene glycol shows the hexagonal (wurtzite) structure of ZnO with crystalline sizes in the range of 32.15-95.37; 35.47-87.20; 40.18-101.20 and 40.18-101.85 nm, respectively. The band gap data of ZnO doped 1, 3, 5, 7% were 2.60, 2.90, 2.99 and 3.01 respectively.

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