PREPARATION AND PROPERTIES OF ZNO NANOPARTICLES

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Abstract

This work deals with the preparation and properties of zinc oxide nanoparticles. Semiconductor ZnO nanoparticles were prepared by thermal annealing at different temperatures and by precipitation reactions including an irradiation induced method of preparation. In the second case zinc acetate was mixed with NaOH under different conditions. Prepared samples were analyzed and characterized by X-ray diffraction, luminescence, transmission and scanning electron microscopy. The crystallite sizes, structure and shape of prepared ZnO nanoparticles were specified.

Keywords: Nanoparticles, zinc oxide, X-ray diffraction, thermal annealing

1. INTRODUCTION

Zinc oxide is a wide-band gap n-type semiconductor due to oxygen vacancies and zinc interstitials. This semiconductor has several favourable properties, including good transparency, high electron mobility and strong room-temperature luminescence [1, 2]. Nanostructures of ZnO can be synthesized into a variety of morphologies, including nanowires, nanorods, tetrapods, nanobelts, nanoflowers, nanoparticles etc. Many methods have been described for the production of ZnO nanomaterials such as laser ablation [3], hydrothermal methods [4], electrochemical depositions [5], thermal annealing [6] and sol-gel methods [7].

One of the most important factors related to ZnO nanoparticles is dependence of their properties on size. The decrease of a semiconductor particle size leads to the increase of its specific surface area and gap energy, which is known as the quantum size effect or quantum confinement. The large surface of nanoparticles results in their high adsorption capacity and catalytic activity.

The aim of this work was to prepare ZnO nanoparticles by different methods and investigate their properties. For this purpose, prepared ZnO powders were characterized by X-ray diffraction, luminescence and transmission electron microscopy. The crystallite sizes, structure and shape of prepared ZnO nanoparticles were specified.

2. EXPERIMENTAL

2.1 Material and chemicals

The used chemicals were of analytical reagent grade: zinc acetate dihydrate and sodium hydroxide, (all from Lachema, Czech Republic). Water deionized by reverse osmosis (Aqua Osmotic, Czech Republic) was used for the preparation of all samples.

2.2 Thermogravimetry

Termogravimetry (TG) analysis was performed on Thermal Analyzer SETSYS-1750 (SETARAM Instrumentation, France) in inert atmosphere of Argon, the heating rate was 10 °C/min and the weight of the sample was 33.26 mg.

2.3 X-ray powder diffraction analysis

X-ray powder diffraction (XRPD) patterns were recorded under CoK_α irradiation (λ = 0.1789 nm) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a fast position sensitive detector VÅNTEC Measurements were carried out in the reflection mode. Powder samples were pressed in a rotational holder.

Phase composition was evaluated using database PDF 2 Release 2004 (International Centre for Diffraction Data).

2.4 Transmission electron microscopy

Transmission electron microscopy (TEM) with high resolution images of ZnO nanoparticles were examined by a JEM 220FS microscope (Jeol, Japan) operating at 200 kV. The nanoparticles were dispersed in ethanol and with ultrasonic sprayer deposited on a TEM grid with carbon holey support film.

2.5 Photoluminescence spectra measurements

Photoluminescence (PL) spectra were measured by a spectrometer FLS920 (Edinburgh Instrument Ltd, UK). The spectrometer was equipped with a 450 W Xenon lamp (Xe900). The excitation wavelength was 365 nm. A width of excitation and emission slits was 3 nm.

2.6 Preparation of nanoparticles

Zinc oxide nanoparticles were prepared by a) thermal annealing of zinc acetate and b) by precipitation reaction of zinc acetate with sodium hydroxide. In the second case zinc acetate was mixed with NaOH under UV irradiation with the maximum emission at 254 nm and the final ratios of Zn : OH were set at 1 : 3. Preparation method of each sample is briefly described in Table 1.

Table 1 Overview of prepared ZnO samples

Number of sample	Method	Temperature/time (°C/h)	Precursors
1	thermal annealing	350/1	zinc acetate dihydrate
2		350/2	
3		350/3	
4		400/1	
5		400/2	
6		400/3	
7		700/3	
8	precipitation reaction + thermal annealing	350/2	zinc acetate dehydrate + sodium hydroxide
9	precipitation reaction + UV irradiation + thermal annealing	350/2	zinc acetate dehydrate + sodium hydroxide

3. RESULTS AND DISCUSSION

3.1 Preparation of nanoparticles

In thermal annealing method 2 g of powdered zinc acetate was annealed at different temperatures for 1-3 hours. After calcination the samples were crushed in a mortar. In the second case ZnO was prepared by the precipitation reaction followed by thermal annealing. Into the stirred solution of 60 ml 3.3 $mmol \cdot l^{-1}$ zinc acetate was added by drop-wise 40 ml 15 $mmol \cdot l^{-1}$ NaOH (flow rate was about 0.67 $ml \cdot min^{-1}$). For the preparation of powder sample, the solution was filtered and the filter cake was subsequently annealed at 350 °C for 2 hours. The third sample was prepared by similar method with the difference that solution was continuously irradiated by an UV lamp.

3.2 Thermal annealing

A sample of zinc acetate dihydrate was analyzed at a heating rate of 10 $°C \cdot min^{-1}$ in an air atmosphere. Measurement was carried out in the temperature range of 50-700 °C. The resulting TGA curve is shown in Figure 1. The initial weight loss of 5.4 mg, which is about 20 % of total weight at 150 °C was due

to dehydration thereby obtaining anhydrous zinc acetate. Subsequent weight loss is due to the formation of zinc oxide. The total weight loss of 26.8 mg (80 %) was finished at the temperature 350 °C.

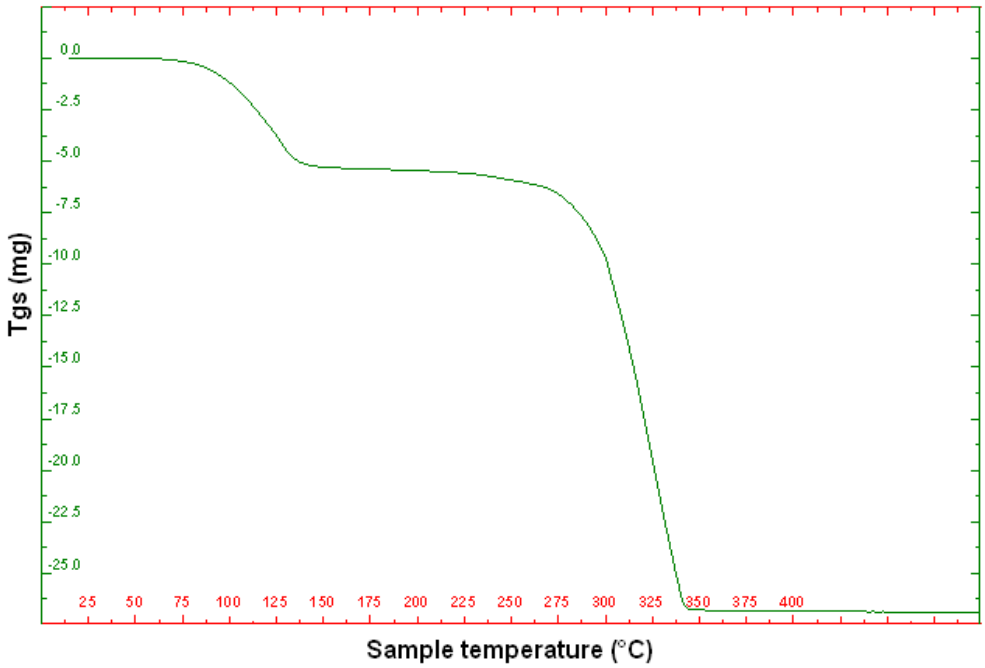

Fig. 1 Thermogravity curve of annealing of zinc acetate dihydrate

Tabel 2 Calculated average crystallite sizes of ZnO by XRPD

Number of sample	**Temperature/time (°C/h)**	**Average crystallite size (nm)**
1	350/1	35.47
2	350/2	35.87
3	350/3	38.62
4	400/1	32.10
5	400/2	37.22
6	400/3	38.33
7	700/3	88.79
8	350/2	38.41
9	350/2	14.76

3.3 X-ray powder diffraction analysis

The X-ray powder diffraction was performed (see Figure 2) and subsequently was found the average crystallite size of ZnO. Measured data of the samples are listed in the following Table 2. All the diffraction peaks (see Figure 2) can be indexed to the hexagonal structure with lattice constants of a = 0.325 nm and c = 0.521 nm from JCPDS card No. 01-70-2551 and no other peaks (impurities) were observed, S.G. = P63mc. From measured data it is obvious that with increasing temperature and time of annealing the average size was increasing. As a result of annealing time the crystallite sized increased up to 20 % which was also observed by other authors [8, 9]. It is also interesting that the smallest crystallite size of 14.74 nm was obtained by the precipitation under UV irradiation. This effect is still unclear and will be further studied.

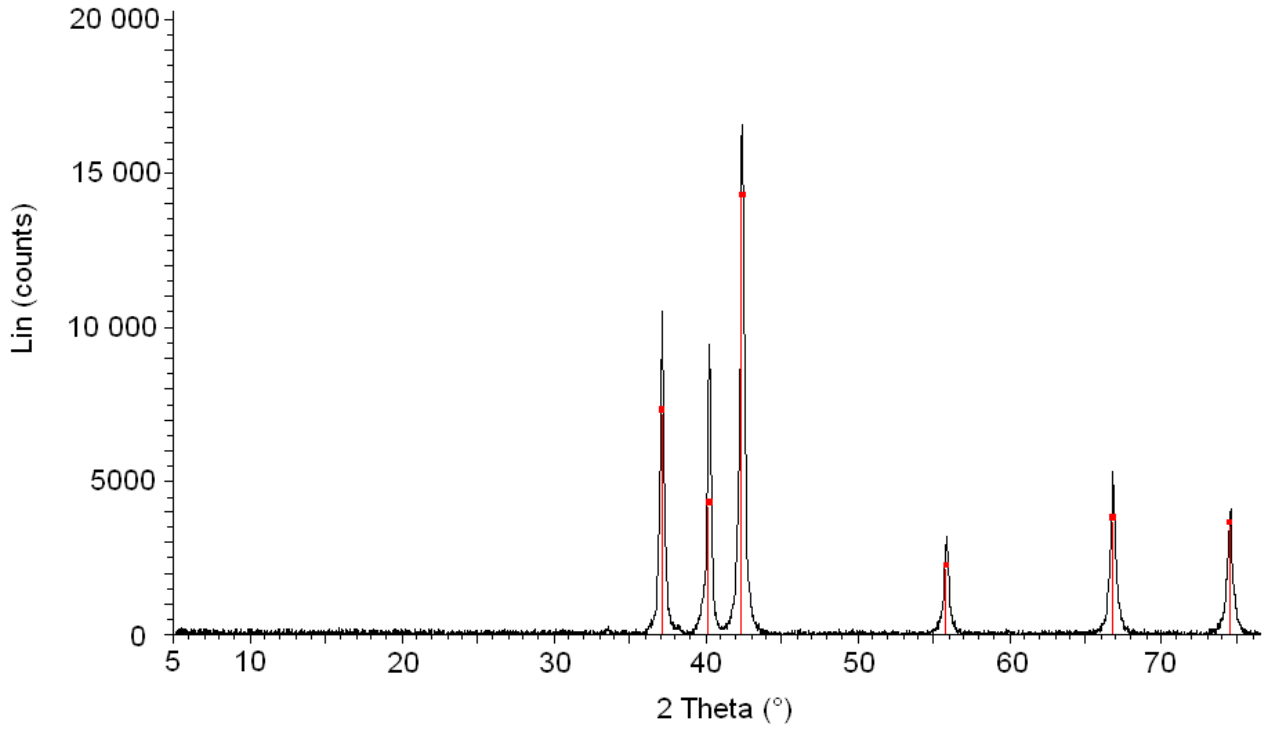

Fig. 2 XRPD pattern of ZnO powder prepared at temperature of 350 °C for 1 h

3.4 Transmission electron microscopy

Statistical analysis from TEM images (see Figure 3) confirmed results of the XRPD analysis and showed that thermal annealing created larger ZnO particles compared to ZnO particles prepared by the precipitation reactions. The mean crystallite size of ZnO nanoparticles prepared by annealing of zinc acetate was about 40 nm and their distribution was very large from 20 nm to 120 nm. On the other hand, the mean size of ZnO crystallites prepared by precipitation with UV irradiation was about 15 nm.

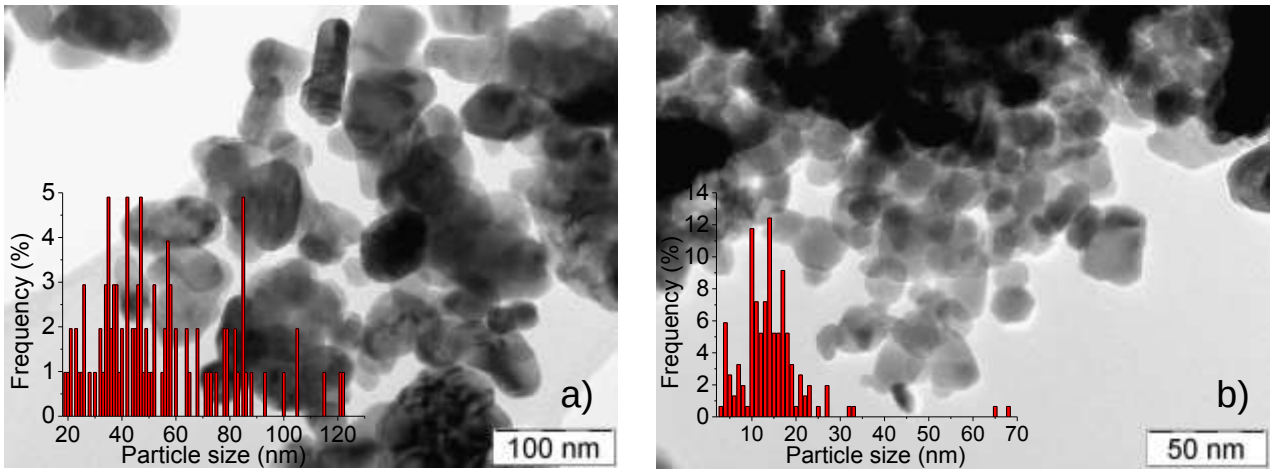

Fig. 3 TEM images of ZnO a) prepared by thermal annealing, b) prepared by precipitation reaction under UV light. Size distribution histograms of ZnO size were placed as insets

3.4 Photoluminescence spectra measurements

Figure 4 shows the PL spectra of ZnO nanoparticles measured at room temperature using Xe lamp as the excitation source. The quantum yield of the PL spectra from ZnO nanoparticles prepared by the thermal annealing was small and the maximum emission was around 520 nm (green emission). ZnO prepared by the precipitation reaction under UV irradiation showed the much higher quantum yield with the maximum emission at 650 nm (orange-red emission). These broad visible emissions are explained to be caused by defects (interstitial Zn, O vacancies) in ZnO structures (green emission) and boundary of

ZnO grains [10, 11]. Therefore we can suppose that these defects were concentrated on surface of small ZnO grains agglomerated into the larger nanoparticles originated by the precipitation.

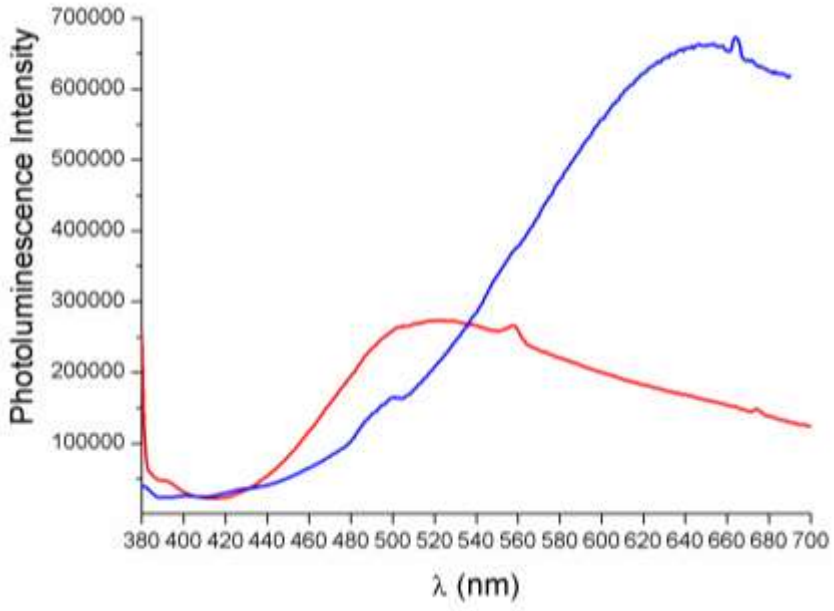

Fig. 4 PL spectra of ZnO nanoparticles. Red line - ZnO prepared by thermal annealing, blue line - ZnO prepared by precipitation reaction under UV irradiation

4. CONCLUSION

ZnO nanoparticles were synthesized by 2 different methods: a) thermal annealing of zinc acetate dihydrate and b) precipitation of zinc ions in aqueous solution with sodium hydroxide. The thermal annealing method gave ZnO nanoparticles larger than the preparation method. This was confirmed by XRPD and TEM images. Also the intensity and positions of broad visible emissions were very different likely as a result of different amounts of oxygen present in both nanostructures. In our research it was observed that temperature and time of annealing had influence on the final particle size: with increasing time and temperature the particles size of ZnO was increasing. The effect of UV irradiation during the precipitation on the ZnO nanoparticles size stayed still unclear and will be studied in near future.

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