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Zinc oxide Ce-doped nanoparticles microwave assisted synthesis with the use of different precursors

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Abstract The study considers the use of various precursors for microwave synthesis of cerium doped zinc oxide nanoparticles its influence on the quality of synthesis. Widely used in various methods precursors were taken for the research. Monohydric and dihydric alcohols – isoamyl alcohol, ethylene glycol, propylene glycol, dipropylene glycol, as well as aliphatic and polycyclic amines – isopropylethylenediamine and urotropine was used for the synthesis of zinc oxide nanoparticles doped with 1% cerium in a mass ratio. The obtained nanoparticles were studied by fluorescence spectroscopy, X-ray diffraction analysis and scanning electron microscopy. It was found that the crystallinity of the obtained samples is $85 \pm 2\%$, while the size of the nanoparticles varies up to 30% depending on the precursor used.

1. Introduction

Zinc oxide is a well-known compound for such scientific applications as nanomaterials, optoelectronics, composite materials, various pigments, piezo electronics, ceramics, catalysts, sensors and etc. Recent years there is an upward trend in researches dedicated to doping zinc oxide by various elements to improve or obtain some new properties of the material. Doped with Cerium zinc oxide nanoparticles could be used as high performance photocatalysts, optical and gas sensors [1-3]. At the same time, there are many different types of synthesis like sol–gel, controlled or direct precipitation, emulsion and microemulsion systems, hydrothermal or solvothermal, microwave and ultrasound synthesis.

Microwave synthesis is distinguished by its high speed and minimal economic cost but as for other methods the result of the synthesis depends on power and time of microwave irradiation, stirring and precursors which could act as structure-controlling agents. In our study, we used 6 different precursors and evaluated their effect on result of the synthesis of zinc oxide nanoparticles doped with cerium under identical conditions.

2. Experiment

The required amount of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Sigma-Aldrich 99.9%) and cerium(III) acetate hydrate ($\text{Ce}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$ Sigma-Aldrich) were used for the preparation of the Ce-doped ZnO nanoparticles. According to dopant's concentration salts mixtures were dissolved in 100ml of distilled water by sonication for 30 min (42 kHz, 60W). The final solution was adjusted to alkaline conditions (pH=8.5) by adding dropwise of aqueous ammonia solution during mixing and



separated for 6 solutions in which 20 μl of following precursors were added: isoamyl alcohol, ethylene glycol, propylene glycol, dipropylene glycol, isopropylethylenediamine and urotropine and treated by microwave irradiation (200 W) for 10 min. Obtained powders were washed with distilled water several times, dried and studied by fluorescence spectroscopy (Shimadzu RF-5301), absorbance spectroscopy (Shimadzu UV1800), XRD (Bruker d8 advance, $\text{Cu K}\alpha = 1.54\text{\AA}$) and SEM (Tescan MIRA3). Bruker Eva 8 and Origin Labs 8.1 software were used for data processing.

3. Results and discussion

Absorbance maximum (Fig.1) was detected at $363\text{ nm} \pm 3\text{ nm}$ for all samples what is equal to 3.17 eV optical band gap according to Tauc's plot calculations and possible because of dielectric properties of cerium oxide [4] and strong UV absorption at far UV region where maximum was impossible to detect according to device detection limit.

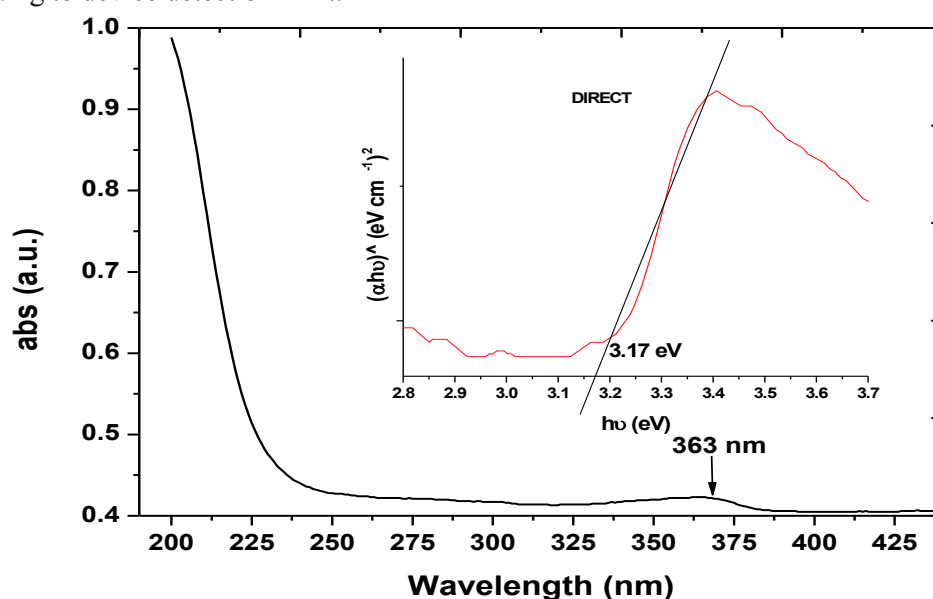


Figure 1. Absorbance spectra of ZnO doped with 1 wt % of Ce with urotropine as precursor and Tauc's plot for direct transitions (on inset)

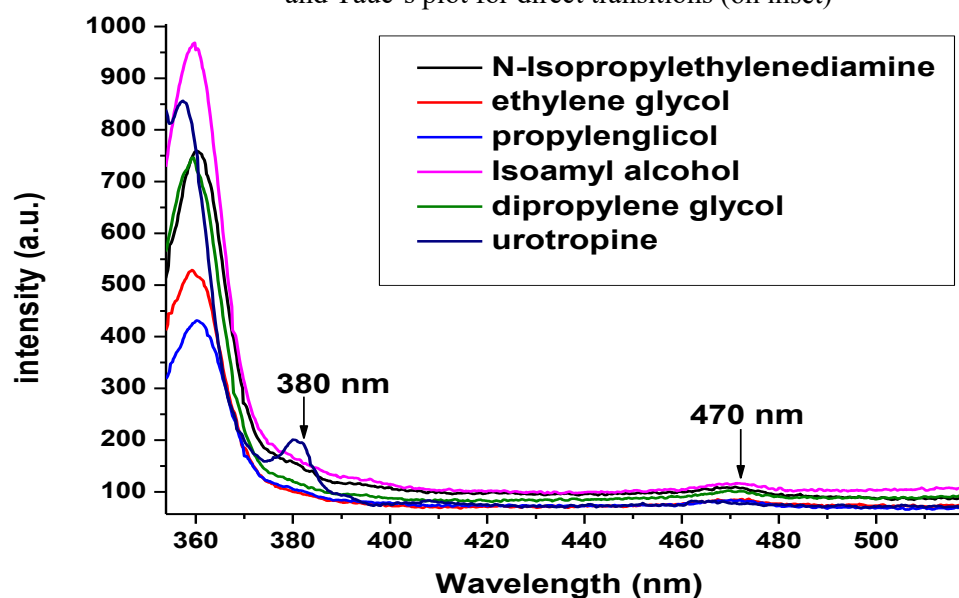


Figure 2. Emission spectra of ZnO doped with 1 wt % of Ce (excitation wavelength = 330 nm)

The emission spectra of zinc oxide can be recorded over a wide range of excitation wavelengths, which was used in an attempt to preliminarily estimate the contribution of precursors to the photoluminescent properties of nanoparticles. Fig.2 shows the PL spectra of the samples measured at the excitation wavelength of 330 nm and the broadband PL spectrum at 380 nm excitation.

PL from the recombination of free or bound excitons at the UV region is different for almost all samples but it could be interpreted as different quality of the crystallites including their size or as for urotropine we supposed that it's residual amount of precursor.

The XRD patterns of the prepared powders (Fig.3) are typical of ZnO powder hexagonal wurtzite crystal structure (JCPDS 01-075-0576). No diffraction peaks associated to Ce or other impurities such as CeO_2 or Ce_2O_3 were identified so it can be concluded that Ce^{4+} ions would uniformly substitute into the Zn^{2+} sites or interstitial sites in ZnO lattice [5]. The morphology of ZnO changes from spherical to rod shaped with the Ce ion doping because the crystal lattice spacing of (100) and (101) crystal face shrinks and (002) expands when Ce substituting for Zn sites what could be seen at the use of urotropine, isopropylethylenediamine, ethylene and propylene glycols [6].

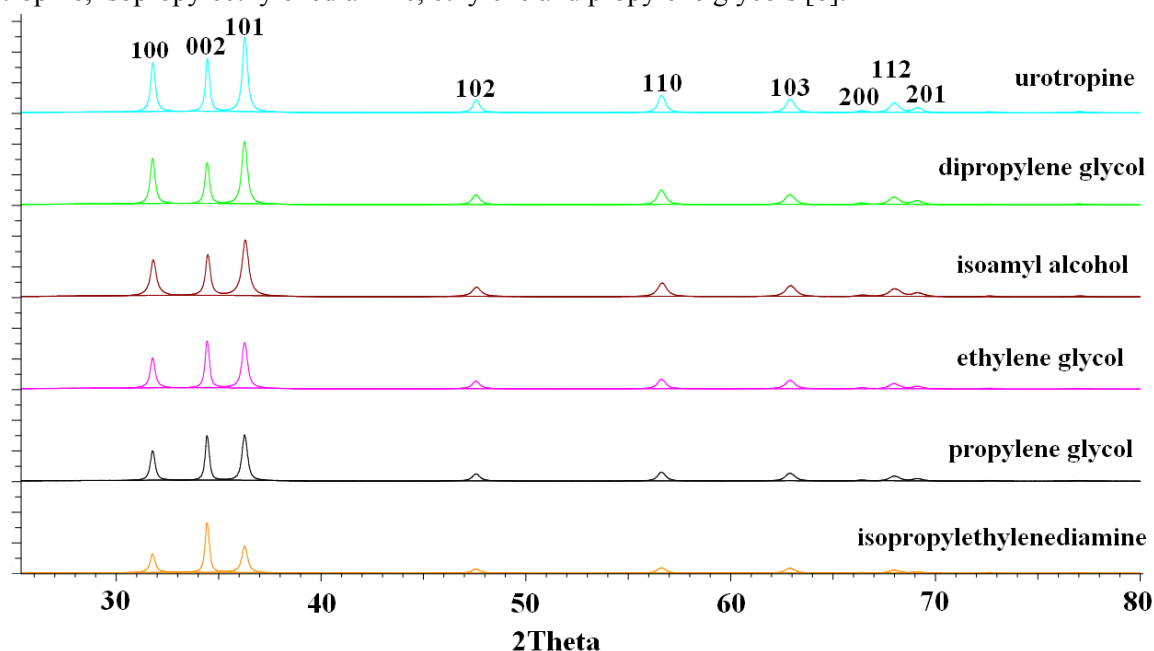


Figure 3. XRD spectra Ce-doped Zinc oxide nanoparticles obtained with different precursors

Crystallinity and average size of the crystallites calculated by peak half-width by Scherrers equation are presented on the table 1. At the same time, we note that no grinding of the samples was carried out and the crystallinity of the samples is really high. Average size mostly depends on time and power of irradiation but in the same conditions of the synthesis it depends on how much cerium entered the crystallite structure what increases the growth of nanorods.

Table 1. Crystallite size by Scherrer Formula and crystallinity of ZnO Ce-doped np's

Precursor	Average size, nm	Crystallinity, %
Isoamyl alcohol	46.8	85.62
ethylene glycol	56.9	85.84
propylenglicol	54.8	86.30
dipropylene glycol	60.5	82.49
Isopropylethylenediamine	55.8	85.65
urotropine	47.8	87.20

Microscopic studies of the samples (Fig.4) showed significant differences between crystallites. It was found that when use isoamyl alcohol, aggregates of nanorods reached 10 μm ; dipropylene glycol - about 5 microns; urotropine (Fig.4 a), isopropyleneethylenediamine, ethylene glycol - about 2 microns. In the case of propylene glycol, nanosized cubes were observed, whose length ranged from 120 to 160 nm and the width from 30 to 74 nm (Fig.4.c). In a more detailed examination of the surface of large particles, nanoscale cubes could be also observed, but only in the case of propylene glycol micron structures consisting of rods are practically not observed. This effect can be explained by the fact that the used precursors are part of the chemical reactions occurring in the synthesis process and they don't reduce particle aggregation only.

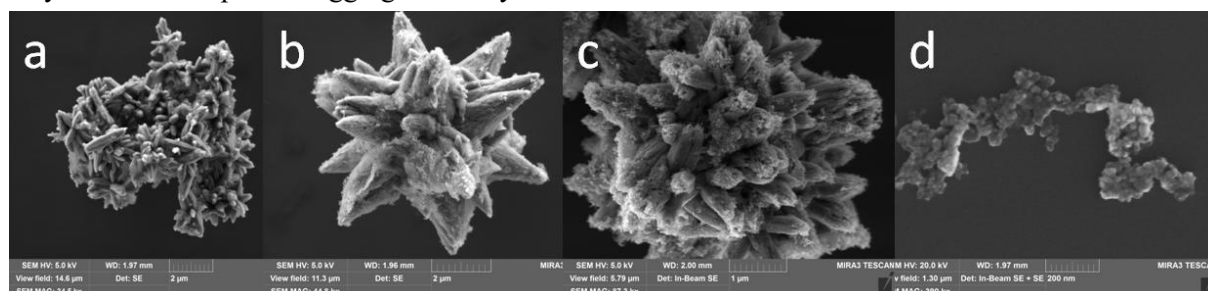


Figure 4. SEM images of ZnO doped with 1 wt% of Ce prepared with different precursors: a) urotropine; b) isopropylethylenediamine; c) isoamyl alcohol; d) propylene glycol;

4. Conclusions

Nanosized structures of zinc oxide doped with cerium using various precursors were obtained by microvawe-assisted method. The effects of precursors on the total amount of dopant in zinc oxide crystallites, crystallinity of the obtained samples, aggregation and crystallite size are established. We conclude that precursors used in this work have chemical or physical interaction with Zn ions during the synthesis which is important for creating a controlled synthesis process.

Acknowledgments

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